STRENGTH AND DURABILITY CHARACTERISTICS OF ALUMINUM JOINTS BONDED BY RUBBER-MODIFIED AND ALUMINUM FILLED EPOXY ADHESIVE

BY

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ABSTRACT

Name: SALAM AL-SHAMMARI

Title: STRENGTH AND DURABILITY CHARACTERISTICS OF ALUMINUM JOINTS BONDED BY RUBBER-MODIFIED AND ALUMINUM FILLED EPOXY ADHESIVE

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The objective of this study was to develop information on the effects of moisture sorption and the filler content on the performance of aluminum joints bonded by rubber-modified and aluminum powder filled epoxy adhesive. Water and fluid immersion tests were utilized to determine the moisture sorption behavior of rubber-modified and aluminum filled epoxy adhesive under complete immersion in distilled water and NaCl solutions. The durability of the adhesive bonded metal joints was investigated by measuring the joint strength by the single lap shear test before and after exposure to three environments: distilled water, sea water and atmosphere.

Moisture diffusion tests show that salt concentration of the exposure solution affects the maximum amount of moisture absorbed by epoxy type A with no rubber content (Lord 309). The lighter the concentration of NaCl solution, the less diffusant absorbed by that adhesive. On the other hand, there appears to be no significant effect of solution salt content on the maximum amount of moisture absorbed by epoxy type B with 40 wt% rubber content (RA-840).

Epoxy type A absorbs larger amount of moisture than epoxy type B in distilled water and lightly concentrated salt solutions. However, the opposite is the case in highly concentrated salt solutions.

Moisture diffusivity in the adhesive increases as the rubber content of the adhesive increases. Consequently, moisture diffusivity is higher in epoxy type B than epoxy type A.

Solution salt content affects the moisture diffusivity in epoxy type A. The higher the salt content in the test solution, the faster the moisture diffusion rate in that adhesive. However, no significant effect of salt concentration on moisture diffusivity was observed in the case of epoxy type B. Moisture diffusivity in epoxy with 9 wt% rubber which is a mixture of both epoxy types is in between those in each epoxy type.

Addition of aluminum particles into the adhesive decreases the amount of moisture absorbed by the adhesive. However, they do not affect the moisture diffusivity in the adhesive significantly.

Mechanical characterization tests show that inclusion of aluminum filler in epoxy adhesive does not affect its adhesive strength and degradation characteristics. Rubber modification of epoxy, on the other hand, does not affect its adhesion strength if not exposed to detrimental environments.

The adhesive strength does not degrade in the Gulf atmosphere for as long as 10 months. However, degradation of the epoxy adhesive with or without rubber content is significant in distilled water and sea water. Inclusion of rubber in the epoxy results in more significant degradation in distilled water. However, it has no significant effect on adhesive degradation in sea water.

MASTER OF SCIENCE DEGREE

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

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ملخص

الاسم سلام خايفة الشمري

عنوان الرسالة خصائص القوى و التحمل لوصلات الألمونيوم المربوطة باللاصق الإيبوكسي المعدل بالمطاط و المحشو بمسحوق الألمونيوم

التخصص هندسة كيميائية

تاريخ التخرج مايو ٢٠٠٦

إن الهدف وراء هذه الدراسة هو تطوير المعلومات عن تأثير امتصاص الرطوبة ومحتوى الحشو على أداء وصلات الألمونيوم المربوطة باللاصق الإيبوكسي المعدل بالمطاط والمحشو بمسحوق الألمونيوم. و قد تم عمل اختبارات الغمر بالماء والسوائل من أجل تحديد سلوك امتصاص الرطوبة في اللاصق الإيبوكسي المعدل بالمطاط و المحشو بمسحوق الألمونيوم في حالات الغمر الكامل في الماء المقطر ومحاليل كلوريد الصوديوم. وأيضا تم فحص مدى قدرة تحمل الوصلات المعدنية المرتبطة بذاك اللاصق عن طريق قياس قوة الوصلات باستخدام اختبار القص التراكبي المفرد وبعد ان تعرضت لثلاث بيئات مختلفة : الماء المقطر وماء البحر وعوامل الجو الخارجية.

وتظهر اختبارات انتشار الرطوبة بأن تركيز الملح في المحلول المعرض يؤثر على الكمية القصوى للرطوبة الممتصة بواسطة اللاصق الإيبوكسي نوع (ا) الغير محتوى علي المطاط نوع (لورد-٣٠٩). ولوحظ أن كلما كانت تركيزات محلول كلوريد الصوديوم خفيفة، كلما قلّ الامتصاص الانتشاري من قبل هذه المادة اللاصقة. وعلى الجانب الآخر، فإنه لا توجد أهمية بالنسبة للرطوبة الممتصة من قبل بواسطة اللاصق الإيبوكسي نوع (ب) المحتوى على نسبة ٤٠% من المطاط نوع (را-٨٤٠).

اللاصق الإيبوكسي نوع (ا) فانه يمتص كمية رطوبة أكبر من اللاصق الإيبوكسي نوع (ب) في الماء المقطر والمحاليل ذات تركيزات ملحية خفيفة ،بينما يكون العكس في حالة المحاليل ذات تركيز ملحية شديدة. حيث يزداد انتشار الرطوبة في المادة اللاصقة كلما ازداد محتوى المطاط في المادة اللاصقة. وبالتالي فإن انتشار

الرطوبة يكون أعلى في اللاصق الإيبوكسي نوع (ب) عنه في النوع (ا).

ويؤثر محتوى الملح في المحلول على انتشار الرطوبة في اللاصق الإيبوكسي نوع (A). ذلك أن كلما احتوى محلول الاختبار على كمية ملح أكثر، كلما كان معدل انتشار الرطوبة أسرع في المادة اللاصقة. بينما لم يتم ملاحظة أي تأثير مهم لتركيز الملح في المحلول على انتشار الرطوبة في اللاصق الإيبوكسي نوع (ب). أما بالنسبة للاصق الإيبوكسي المحتوى علي المطاط بنسبة ٩% (هو عبارة عن مزيج بين نوعي الإيبوكسي) فان انتشار الرطوبة يكون في يكون بين كل نوع من الإيبوكسي.

وجد أن إضافة جزيئات الألمونيوم في المادة اللاصقة يعمل على تقليل كمية الرطوبة الممتصة من قبل المادة اللاصقة. بينما لا تؤثر على انتشار الرطوبة في المادة اللاصقة بشكل ملحوظ.

وتظهر اختبارات الوصف الميكانيكي أن إدراج الحشو الألمونيوم في اللاصق الإيبوكسي لا يؤثر على قوة المادة اللاصقة ولا علي خصائص انحلالها. وأما على الجانب الآخر ، فان اللاصق الإيبوكسي المعدل بالمطاط لا يؤثر على قوة اللصق لديها ، أذا لم تتعرض إلى بيئات قاسية.

قوة اللاصق لا تتحلل أذا ما تعرضت لأكثر من ١٠ شهور في جو الخليج. بينما التحلل في اللاصق اللإيبوكسي المحتوى أو الغير محتوى على المطاط يكون ذا أهمية في الماء المقطر أو ماء البحر. وجود المطاط في اللاصق الإيبوكسي يؤدي إلى تحلل واضح في الماء المقطر ،و لكن لا يكون هناك أي تأثير واضح على تحلل اللاصق اللإيبوكسي في ماء البحر.

درجة ماجستير في العلوم
جامعة الملك فهد للبترول والمعادن
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1. INTRODUCTION

The use of adhesives is widespread and growing from the high-technology aerospace industries into all types of general engineering applications. Some advantages of adhesive bonding over the common mechanical joining techniques such as riveting and welding are lightness, neatness, simpler design, increased fatigue and corrosion resistance, and reduced costs [Kozma and Olefjord, 1987a; Eagland, 1990; Watson, 1987]. Many spot-welded automotive parts are being replaced by adhesive-bonded components because of the difficulties encountered in welding of galvanized or coated steels [Tai and Szklarska-Smialowska, 1993a].

The resins which form the mainstay of the adhesive industry are the epoxies. Epoxies are able to bond well to a variety of treated or untreated metal surfaces [Mohan, 1990]. In aircraft manufacture, there is a great need for evenly stressed, smooth bonding of thin aluminum sheet and honeycomb materials. Epoxy adhesives have a good affinity for aluminum alloy surfaces, and the oxide layers produced during surface preparation [Chasser, et al., 1993]. Epoxy resins are thermosets with extraordinary adhesion accompanied by simple cures, good strength, creep resistance, heat resistance, chemical durability and relatively low shrinkage [Chan, et al., 1984; Tai and Szklarska-Smialowska, 1993a; McEwan, et al., 1999].

In spite of their superior properties, epoxy resins are brittle and liable to cracking. Their crack resistance can, however, be improved by including a toughening agent, such as liquid rubber, prior to curing. In the curing stage micro-phase separation occurs with small rubber-rich domains dispersed within the epoxy matrix. The rubber particles act as shock absorbers resulting in a large increase in fracture energy absorption [Chan, et al., 1984;

Eagland, 1990; McEwan, et al., 1999]. Rubber-modified epoxy resin is widely employed as a base for adhesive compositions. A commonly used rubber for epoxy toughening is carboxy terminated butadiene acrylonitrile (CTBN) [Chan, et al., 1984; McEwan, et al., 1999]. In practice, elastomer concentrations of 5% to 15% by weight are commonly used [Farris, 2002].

In a variety of industrial applications epoxy adhesives are required to have an enhanced thermal conductivity. The normal method for changing this physical property is to add to the epoxy a filler of higher conductivity than the continuous phase [Tai and Szklarska-Smialowska, 1993a; Hermansen and Tunick, 1989; Tomlinson and Stapley, 1977; Lee and Neville, 1967; Kingery, 1960; Nieberlein and Steverding, 1977; Gaynes, et al., 1997; Hahn, et al., 1998; Subramanian, et al., 1998; Nikkeshi, et al., 1998]. By the incorporation of fillers into the adhesive, the resin content (and thus the cost) is also reduced.

Achieving improved thermal conductivity is dependent on filler selection and loading level. Filler type, size, shape and volume fraction determine the adhesive thermal conductance. The factor increases with increasing volume fraction of filler and high aspect-ratio particles increase thermal conductivity more effectively than spherical particles. Theoretically, the thermal conductivity of the filler is not an important variable except when it is within a factor of 10 of the thermal conductivity of the polymeric matrix (adhesive). Most metal fillers have thermal conductivities greater than 10 times the matrix thermal conductivity [Hermansen and Tunick, 1989].

Alumina powder is a commonly used filler for improving the thermal conductivity of adhesives used as dielectrics (electrically insulative adhesives). Silver powder or flakes are

commonly used to improve the thermal conductivity and attain electrical conductivity for adhesives intended to be an electrical path [Hermansen and Tunick, 1989; Kang and Purushothaman, 1998; Lu, et al., 1999]. The filler level must be sufficiently high to achieve point-to-point contact before electrical conductivity is attained [Hermansen and Tunick, 1989]. However, too high filler content might cause a degradation in mechanical properties of the adhesive [Nikkeshi, et al., 1998]. There are also several commercially available epoxy adhesives reinforced with other metal fillers such as aluminum powder.

Upon deleterious environmental exposures, durability of adhesive-bonded structural joints can be seriously influenced. Especially moisture and aggressive ion ingress into the bonded joint are primary causes of adhesive bond degradation [Tai and Szklarska-Smialowska, 1993a; Kinloch, 1983; Shaffer, et al., 1992; Brewer, 1988; Tai and Szklarska-Smialowska, 1993b; Prakash, et al., 1987; Stevenson and Priest, 1991; Kim and Ajersch, 1994; Comyn, 1983; Xiao and Shanahan, 1997; Srivastava and Hogg, 1998; Moidu et al., 1998; Lindberg, 1992]. Water may enter a joint by diffusion through the adhesive, by transport along the adhesive-adherend interface and by capillary action through cracks in the adhesive. Once inside a joint, it may cause strength degradation by inducing changes in the physical properties of the adhesive and/or degrading the chemical bond between the adhesive and the metal and/or inducing stresses in joints by nonuniform swelling of the adhesive [Comyn, 1983; Srivastava and Hogg, 1998; Moidu et al., 1998; Srivastava, 1999].

The objective of this study was to explore the effects of the addition of CTBN and aluminum particles to the epoxy adhesive on its adhesion strength, durability characteristics and water uptake properties.

2. BACKGROUND

2.1 ADHESION AND ADHESIVES

An adhesive may be defined as a material which when applied to surfaces of materials can join them together and resist separation. Adhesive is the general term and includes cement, glue, paste, etc. The term adhesion is used when referring to the attraction between the substances. The materials being joined are commonly referred to as the substrates or adherends, and the latter term is particularly convenient when the materials are part of a joint [Kinloch, 1983].

Structural (load bearing) adhesives are extensively used in the aerospace industry to join metals such as aluminium, titanium and their respective alloys and, increasingly, fiber-laminate adherends, such as carbon-fiber (cfrp) and glass-fiber (grp) reinforced plastics. However, they are also widely used in the general engineering and construction industries where, apart from the adherends listed above, wood and concrete are also frequently bonded using such adhesives [Kinloch, 1983; Shaffer, et al, 1992; Ivanova, et al, 2000; Prakash, et al, 1987; Chasser, et al, 1993].

Structural adhesives are often based upon low molar-mass phenolic or epoxy resins, and more recently acrylic resins, which polymerize or cure (this process is also sometimes known as hardening), to give highly crosslinked adhesives, i.e. thermosetting polymers, which have chemical bonds connecting the polymer chains. These resins have gained wide acceptance for several reasons. For example, the resins initially possess a sufficiently low viscosity (although in some instances heat may be required) to flow over a substrate surface without the need to employ solvents. Also, a variety of curing agents may be used, particularly in the case of epoxy resins, to give a wide range of possible times and

temperatures for the curing reaction. Upon curing, these resins possess a high degree of crosslinking and high modulus, high strength, low creep and good elevated-temperature properties. However, this chemical structure often produces a very brittle adhesive exhibiting a poor crack resistance. Therefore, it is usually necessary to increase the toughness of such adhesives if they are to be successfully used in structural applications and this is frequently achieved by the controlled inclusion of rubber, which phase-separates when the resin is cured, to give a two-phase microstructure. The microstructure enables the good physical properties resulting from the high crosslink density in the cured resin phase to be maintained whilst the presence of the dispersed rubbery second phase greatly increases the toughness and peel strength of the adhesive. The adhesives are also usually formulated with metal fillers to improve their thermal conductivity [Hermansen and Tunick, 1989; Tomlinson and Stapley, 1977; Gaynes et al., 1997; Hahn et al., 1998; Subramanian et al., 1998; Nikkeshi et al., 1998; Kinloch, 1983; Lee and Neville, 1967; Kingery, 1960; Nieberlein and Steverding, 1977].

One of the most important requirements of structural adhesive joint is the ability to retain a significant proportion of its load-bearing capability for long periods under the wide variety of environmental conditions which are likely to be encountered during its service life. Unfortunately, one of the most hostile environments for structural adhesive joints is water and this, of course, is one of the most commonly encountered. Indeed, by far the most important problem currently facing adhesive scientists and technologists is that of the long-term durability of structural adhesive joints exposed to environments where the concentration of liquid water, or water vapor, is relatively high [Kinloch, 1983]. This matter will be discussed in more detail later.

2.2 MECHANISM OF ADHESION

The mechanisms of adhesion are still not fully understood and many theories are to be found in the current literature. Some of the proposed theories are presented below.

2.2.1 Mechanical Interlocking

This theory proposes that mechanical keying, or interlocking, of the adhesive into the irregularities of the substrate surface is the major source of intrinsic adhesion. However, the attainment of good adhesion between smooth surfaces exposes this theory as not being of general applicability. Moreover, the enhancement of joint strength that may sometimes result from increasing the rugosity of the adherend surface appears often to result from other factors, e.g. an increase in surface area, improved kinetics of wetting or an increase in the extent of plastic deformation of the adhesive [Kinloch, 1983].

2.2.2 Diffusion Theory

The diffusion theory of adhesion states that the intrinsic adhesion of high polymers to themselves (autohesion), and to each other, is due to mutual diffusion of polymer molecules across the interface. This requires that the macromolecules or chain segments of the polymers (adhesive and substrate) possess sufficient mobility and are mutually soluble, i.e. they possess similar values of the solubility parameter. The solubility parameter, δ, may be defined by:

$$\delta = \left(\frac{\Delta H_V - RT}{V} \right)^{\frac{1}{2}} \qquad (1)$$

where ΔH_v is the molar heat of vaporization, R is the gas constant, T is the temperature (K) and V is the molar volume.

The above conditions are usually met in the autohesion of elastometers and in the solvent welding of compatible, amorphous plastics. In both these examples interdiffusion does significantly contribute to the intrinsic adhesion. However, where the solubility parameters of the materials are not similar, or where one polymer is highly crosslinked, is crystalline or is above its glass transition temperature, then interdiffusion is an unlikely mechanism [Kinloch, 1983].

2.2.3 Electrostatic Theory

If the adhesive and substrate have different electronic band structure there is likely to be some electron transfer on contact which will result in the formation of a double layer of electrical charge at the interface. The electrostatic theory of adhesion suggests that the electrostatic forces arising from such contact or junction potentials may contribute significantly to the intrinsic adhesion. However, this theory has been largely discredited and the current view is that interfacial forces arising from any electrical double layer between the adhesive and adherends do not make a major contribution to the intrinsic adhesion [Kinloch, 1983; Allen, 2003].

2.2.4 Physical Adsorption Theory

The adsorption theory of adhesion is the most generally accepted one [Kinloch, 1983]. This theory proposes that, provided sufficiently intimate intermolecular contact is achieved

at the interface, the materials will adhere because of the surface forces acting between the atoms in the two surfaces; the most common such forces are Van der Waals forces and are referred to as secondary bonds [Kinloch, 1983; Allen , 2003]. Adsorption involves interactions between dipoles of various types and fall into three groups [Allen, 2003]:

i. *Dipole/dipole interactions - Keesom forces*: This first group arises from the interaction and attraction of pairs of molecules which both have permanent dipoles.

ii. *Dipole/induced dipole interactions - Debye forces*: The second group arises when a molecule with a permanent dipole approaches a molecule with no dipole and induces a temporary dipole in the neutral molecule and then an attraction arises.

iii. *Molecule/molecule interaction - London Dispersion forces*: The third group are universal, causing attraction between every pair of non-polar particles which approach each other sufficiently closely, irrespective of any recognisable dipoles. They arise from the instantaneous quantum mechanical asymmetry of the electron clouds and hence transitory dipoles which interact.

The potential energy of each of these has a similar pattern:

$$E = \frac{k}{r^6} \tag{2}$$

where E is the potential energy of a pair of molecules, k is a term involving both universal constants and parameters characteristic of the particular pair of molecules, r is the distance of separation of the molecules.

Thus, the potential energy, and hence the attractive force, decreases very sharply as the distance of separation of molecules increases – doubling the separation reduces the energy of interaction to a sixty–fourth [Allen, 2003].

2.2.5 Chemisorption Theory

In addition to secondary Van der Waals interactions, chemisorption may well occur and thus ionic, covalent and metallic bonds may operate across the interface; these types of bonds are referred to as primary bonds [Kinloch, 1983; Allen , 2003].

2.2.6 Pressure Sensitive Adhesives

While the pressure sensitive adhesives are very familiar as adhesive tapes for many domestic as well as commercial purposes, they are quite different in their nature from all the other adhesives. They depend upon remaining as a stable liquid of very high viscosity, perhaps of the order of 10 Pa s. They have to retain this viscosity throughout their useful life, never curing or cross linking. The strength of their bond depends upon the pressure with which they are applied, because it all depends upon the flow under pressure of this highly viscous liquid to bring it into intimate contact with the adherend surface. To break the bond and separate the tape from the adherend requires the adhesive to flow in the opposite direction and eventually to yield. If it undergoes cross linking, as can easily happened if the tape is exposed to bright sunlight, then it becomes hard and brittle, the bond ceases to exist and the backing can be lifted away [Allen, 2003].

2.2.7 Weak Boundary Theory

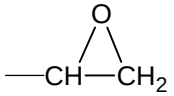
While strictly not a theory of adhesion, the weak boundary layer theory proposes that clean surfaces can give strong bonds to adhesives, but some contaminants such as rust and oils or greases give a layer which is cohesively weak. However, not all contaminates will form weak boundary layers, as in some circumstances they might be dissolved by adhesive [Comyn 1997; Allen, 2003].

2.3 EXPOXY-BASED ADHESIVES

Epoxies are the best known and most widely used structural adhesives. They are also used as matrix-resins for fiber-reinforced composites and as surface coatings. Epoxy compositions are made up of the resins themselves plus the hardeners that produce the curing reactions resulting in a cross-linked structure. There are only a few commercial epoxide resins, but they can be mixed with a wide range of hardeners, which include amines and acid anhydrides. An advantage is that no volatiles are formed on hardening/curing and shrinkage is very low. There might be other modifying adjuncts that can be present such as fillers, additives and co-reacting resins [Comyn 1997; Dow Plastics, 1999].

2.3.1 Epoxy Resin

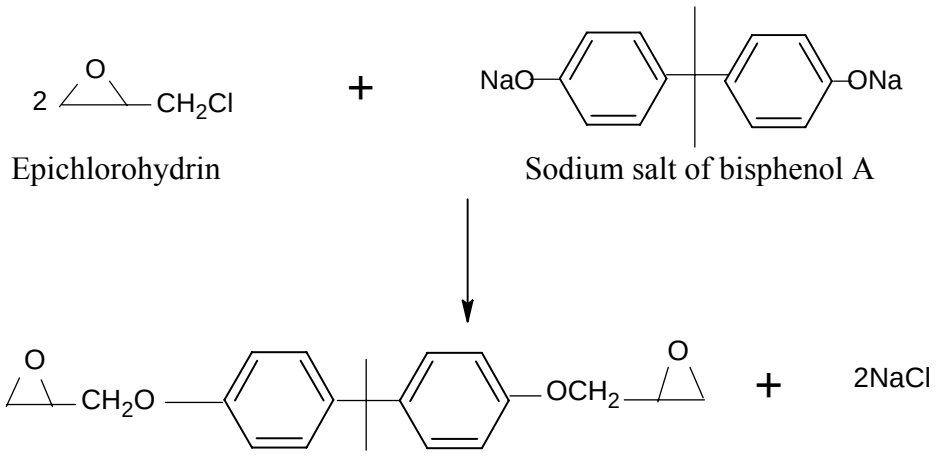
Epoxy resins contain a reactive oxirane structure



(3)

which is commonly referred to as “epoxy” functionality. Liquid epoxy resins are converted through these reactive epoxy sites into cohesively strong solids [Dow Plastics, 1999].

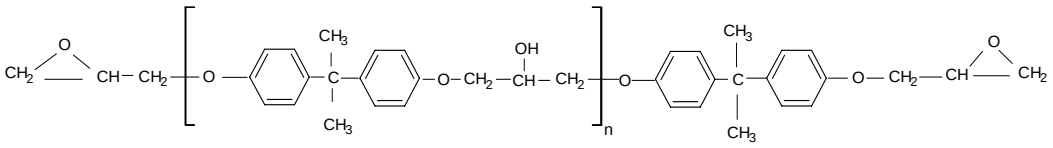
The most commonly used epoxy resin is (2,2-bis[4-(2^{l}3^{l} epoxy propoxy) phenyl] propane), commonly named the diglycidyl ether of bisphenol A (DGEBA), and it is made by reacting the sodium salt of bisphenol A with epichlorohydrin [Comyn, 1997].



Epichlorohydrin Sodium salt of bisphenol A (4)

Diglycidyl Ether of Bisphenol A (DGEBA)

The higher molecular weight homologs are represented by the following theoretical structure:



(5)

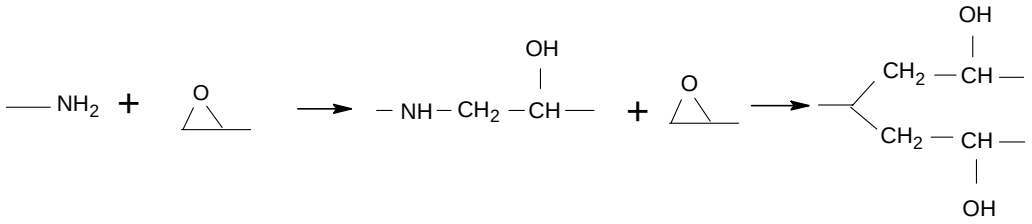
General Chemical Structure of Bisphenol A Epoxy (DGEBA) Resin

With increasing molecular weight, another reactive site - the OH group - is introduced. This group can react at higher temperatures with anhydrides, organic acids, amino resins, and phenolic resins or with epoxide groups (when catalyzed) to give additional cross-linking [Dow Plastics, 1999].

2.3.2 Hardeners/Curing Agents

There are many materials suitable as reactive cross-linking agents for epoxy resins. The most common types of curing agents are primary and secondary polyamines and their adheats, anhydrides, polymides and catalytic types [Comyn 1997; Dow Plastics, 1999].

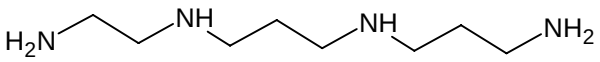
Both aromatic and aliphatic amines are used as hardeners, and the stoichiometry is that one epoxy ring will react with one amine-hydrogen atom in a condensation polymerization. The reaction of a primary amine group with epoxide ring is shown below [Comyn, 1997]:



(6)

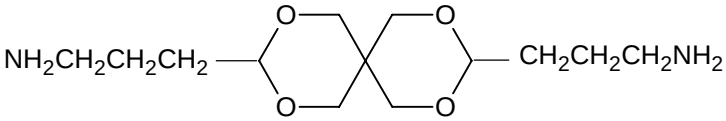
Reaction of a Primary Amine With 2 Epoxy Groups

Some typical aliphatic amine curing agents are triethylenetetramine (TETA), which is six-functional (Structure 7) and 3,9-bis-(aminopropyl)-2,4,8,10-tetraoxaspiro[5.5]undecane which is four-functional (Structure 8).



(7)

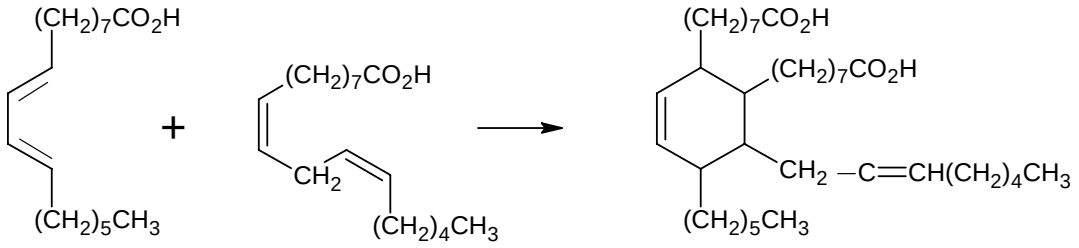
Triethylenetetramine (TETA)



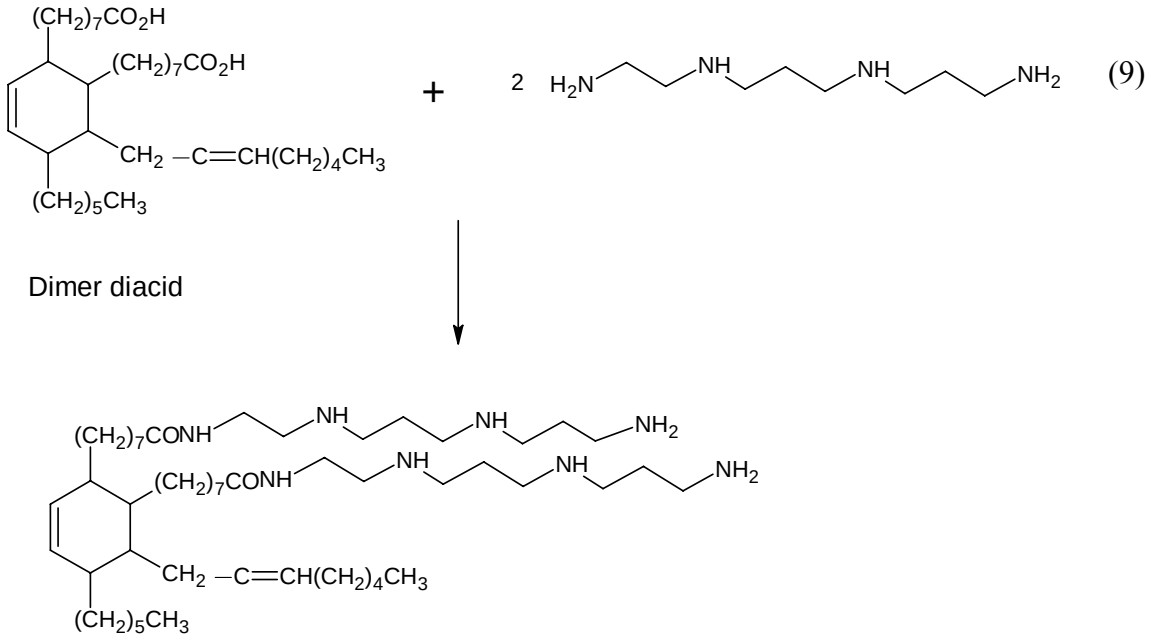
(8)

3,9-Bis-(aminopropyl)-2,4,8,10-tetraoxaspiro[5.5]undecane

The volatility of polyamine hardeners such as TETA can be a source of irritation, and this can be reduced by reacting them with some dicarboxylic acids as shown in Scheme 9. Such compounds are often known as Versamids [Comyn, 1997].



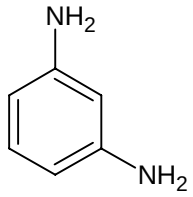
Linoleic acid



Versamid Hardener

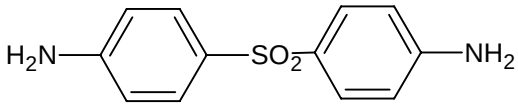
Epoxy adhesives with aliphatic amines can be cured at room temperature or the process can be accelerated by heating. Typical cure times are 14 hours at room temperature

or 3 hours at 80°C. Curing with aromatic amines requires elevated temperatures, typically 2 hours at 150°C, and the cured adhesives have higher glass transition temperatures and the joints tend to be more durable. Some aromatic amine hardeners are shown below [Comyn, 1997]:



(10)

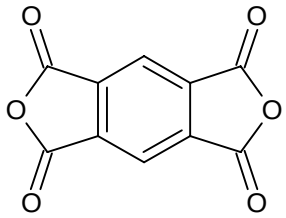
1,3-Diaminobenzene



(11)

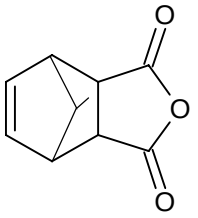
4,4'-Diaminodiphenyl Sulfone

Curing with acid anhydride hardeners is also by condensation polymerization and requires elevated temperatures. Two examples are pyromellitic dianhydride (Structure 12) and methyl nadic anhydride (Structure 13) where the product groups are esters. If the parent acids were used, a disadvantage is that water would be produced [Comyn, 1997].



(12)

Pyromellitic Dianhydride



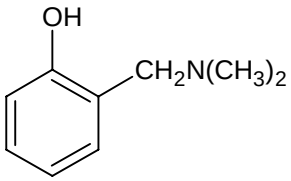
(13)

Methyl Nadic Anhydride
(*7-Methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Anhydride*)

One-part adhesives can be made with hardeners, which require elevated temperatures. Such a hardener is dicyandiamide ($H_2N–C(=NH)–NH–CN$), which has the added advantage of being insoluble in DGEBA at room temperature, dissolving when adhesive is heated. Such adhesives are often supplied in the form of a film, which is stored in a refrigerator, and often contains a textile fabric or carrier to assist in handling the adhesive and in controlling glue-like thickness [Comyn, 1997].

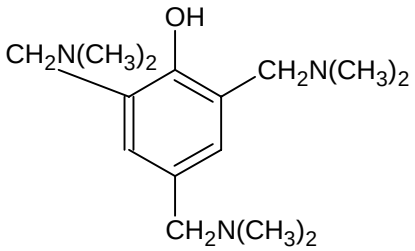
Rapid curing epoxy adhesives employ polythiol hardeners containing $CH(OH)CH_2SH$ groups, in which the hydroxyl groups activate the thiol groups by hydrogen bonding. Such adhesives cure within a few minutes at room temperature [Comyn, 1997].

All the hardeners mentioned so far react with resin by condensation polymerization. Addition polymerization by ring-opening epoxide groups is initiated by tertiary amines and some complexes of boron trifluoride. The most frequently used tertiary amines are shown below [Comyn, 1997]:



(14)

2-(Dimethlaminomethyl)phenol



(15)

2,4,6 Tris-(dimethlaminomethyl)phenol

2.4 KINETICS AND MECHANISM OF MOISTURE DIFFUSION IN POLYMERS

Diffusion of liquid in polymer can be visualized as a series of jumps in which Brownian motion of chain segments of the polymer produces transient voids in the vicinity of the liquid penetrant, enabling it to move within the polymer. Of course, the size of the molecule of liquid is related to the size of the void required to enable a jump. The temperature dependence of diffusivity is described by the Arrhenius law, and the activation energy is related to the amount of energy required for the process of diffusion [Vergnaud, 1991].

The amount of substance diffusing in the *x*-direction across a plane of unit area in unit time is known as the flux, and is related to the concentration gradient $\partial c/\partial x$ by Fick's first law,

$$j_x = -D\frac{\partial c}{\partial x} \tag{16}$$

This can only be directly applied to steady-state diffusion, where concentrations at points within the system are not varying with time; this is clearly not the case when uptake is occurring. The build-up or decay of a diffusing species in a small-volume element is given by Fick's second law, which can be derived from the first law. The derivation considers that the change of concentration with time in the element is controlled by the fluxes crossing its faces. In Cartesian co-ordinates Fick's second law is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D_x \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_y \frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(D_z \frac{\partial c}{\partial z}\right) \tag{17}$$

If diffusion is restricted to the *x*-direction, such as is the case presented by a thin film absorbing a fluid, where diffusion into the edges of the film can be ignored, the second law can be simplified to [Kinloch, 1983]

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D_x \frac{\partial c}{\partial x} \right) \tag{18}$$

If by some convenient experimental arrangement, the concentrations just within the surfaces of a plane sheet of thickness, l, are maintained constant, the amount of diffusant, M_t, taken up by the sheet in a time, t, is given by the equation [Crank and Park, 1968]

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{l^2}\right)^{\frac{1}{2}}\left(\frac{1}{\pi^{\frac{1}{2}}} + 2\sum_{n=0}^{\infty}(-1)^n \, ierfc \ \frac{nl}{2(Dt)^{\frac{1}{2}}} \right) \tag{19}$$

The uptake is considered to be a diffusion process controlled by a constant diffusion coefficient, D, and M_∞ is the equilibrium sorption attained theoretically after infinite time. Equation 19, with suitable interpretation of M_t, and M_∞, also describes desorption from the same sheet, initially conditioned to a uniform concentration, whose surface concentrations are instantaneously brought to zero or some lower value at $t = 0$. The value of D can be deducted from an observation of the initial gradient of a graph of M_t/M_∞ as a function of $(t/l^2)^{1/2}$. This observation is made easier by the fact that, for a constant diffusion coefficient, the graph for a sorption experiment is a straight line, to within the normal limits of experimental error, for M_t/M_∞ as much as about 50 percent. That is, at short times, where M_t/M_∞ is less than 0.5, Equation 19 can be approximated by the following [Crank and Park, 1968].

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{\frac{1}{2}} \tag{20}$$

Although analytical methods for obtaining expressions for the sorption rate from Fick's equations are not possible when D is a function of the concentration, Equation 20 can be used as an initial sorption law but with D substituted by $\overline{D}$ where $\overline{D}$ represents some kind of average diffusion coefficient. It turns out, however, that Equation 20 holds up to higher values of M_t/M_∞ when the diffusion coefficient increases with concentration, while for D decreasing with increasing concentration, M_t/M_∞ is only proportional to $t^{1/2}$ over the very initial region of the sorption [Crank and Park, 1968].

Another form of equation describing sorption and desorption (for the boundary conditions) is [Crank and Park, 1968]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left[-\frac{D(2m+1)^2\pi^2 t}{l^2}\right] \tag{21}$$

This equation is most suitable for moderate and large times at which it can be approximated by the following

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}e^{-\frac{D\pi^2 t}{l^2}} \tag{22}$$

That is, at large times, a plot of $\ln(1-M_t/M_\infty)$ *vs.* (t/l^2) *gives* a straight line with a slope of $-D\pi^2$ from which D, assumed constant, can be determined.

Another way of determining D from Equation 21 is given by Crank and Park (1968) as follows. From Equation 21, the value of t/l^2 for which $M_t/M_\infty = \frac{1}{2}$, conveniently written as $(t/l^2)_{\frac{1}{2}}$ is given by

$$\left(\frac{t}{l^2}\right)_{\frac{1}{2}} = -\frac{1}{\pi^2 D}\ln\left[\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right] \tag{23}$$

Approximately, the error being about 0.001 percent. Thus we find

$$D = \frac{0.04919}{\left(t / l^2\right)_{\frac{1}{2}}} \tag{24}$$

and so, if the half-time of a sorption or desorption process is observed experimentally the value of the diffusion coefficient, assumed constant, can be determined.

In the majority of studies, water sorption in adhesive materials occurs according to Fick's law [Tai and Szklarska-Smialowska, 1993a; Ivanova et al., 2000; Brewer et al., 2000; Hussain and Niihara, 1999]. In some cases, however, the complex water-sorption phenomenon in polymers can lead to various kinds of anomalies including a second mechanism such as a chemical reaction [Ivanova et al., 2000; Soles et al., 2000; Roy, et al., 2000; Tai and Szklarska-Smialowska, 1993a].

2.5 SURFACE PREPARATION OF ADHESIVELY BONDED JOINTS

The way in which surfaces are prepared varies with the materials being bonded. A great deal of research is taking place in the bonding of steel and aluminum, because these materials are widely used in automotive and aircraft industry [Kozma and Olefjord, 1987a; Eagland, 1990; Watson, 1987; Kinloch, 1987; Kozma and Olefjord, 1987b; Brewis, 1985; Hogg and Janardhana, 1993; Katz and Bron, 1991; Tai and Szklarska-Smialowska, 1993a; Chasser, et al., 1993; Mohan, 1990; Thrall, 1979]. In bonding steel, there is a problem with oxide adhesion to the base metal. Rust separates readily from iron, and is therefore detrimental to the strength of an adhesive joint. In the case of aluminum, in a humid environment, no stable oxide is formed on the surface. The joints with corroded substrate oxide always fail in the oxide.

To be able to obtain a strong and stable bond between the metal and the adhesive, the natural surface oxide should be removed and replaced with a new, continuous, solid, corrosion resistant oxide layer. The removal can be done mechanically and/or chemically. Mechanical (abrasive) cleaning also increases the surface roughness and, consequently, the bond strength by mechanical interlocking and by the increased number of chemical bonds on the larger surface area. Also, various chemical treatments, the most common being acid etches, have been developed to modify the oxide, to render it more receptive to bonding [Kozma and Olefjord, 1987a, 1987b; Brewis, 1985; Hogg and Janardhana, 1993; Kinloch, 1983].

A preferable method is the anodizing treatment, in which the metal is immersed in various concentrations of acids (such as phosphoric or chromic) while an electrostatic charge is applied [Brewis, 1985; Katz and Bron, 1991]. The oxide reacts with the etchant to

form a compound which is higher in surface energy. In this way, the metal oxide is rendered much more receptive to bonding.

However, often in industrial practice, although the benefits of surface preparation are widely known, it is not done properly for economic and safety reasons. Proper surface preparation takes extra production time, tends to be labor intensive, and usually involves use of hazardous materials. Hence, an industrial structural adhesive must be suitable for use on less than ideal surfaces.

3. EXPERIMENTAL

3.1 APPROACH

The choice of which adhesive to use in an industrial application requires assessment of its behavior in the real service environment. This assessment involves exposure of the adhesive to the simulated environment for a certain period, and evaluation of the exposed adhesive for changes in properties. Water and fluid-immersion tests have been widely utilized to evaluate changes in the properties of adhesives [Tai and Szklarska-Smialowska, 1993a]. Water-immersion tests are performed by immersing specimens in distilled water and fluid-immersion tests are performed by immersing specimens in a fluid to which the adhesive may be exposed to during industrial use [Cagle, 1968]. A sodium chloride solution is the most commonly utilized test solution for testing adhesively bonded automotive joints. Both the water- and fluid-immersion tests are effective techniques in evaluating the properties of adhesives such as the absorption rates of solutions in adhesives, the stability of adhesives, swelling of adhesives, color changes in adhesives, and delamination of adhesives from metal adherents [Cagle, 1968; Tai and Szklarska-Smialowska, 1993a].

The emphasis was placed upon determining the moisture sorption behavior of rubber modified and aluminum powder filled epoxy adhesive under complete immersion in distilled water and NaCl solutions. The water uptake rate of the adhesives was measured as a function of the filler content, concentration of the sodium chloride solution and exposure time.

The traditional evaluation of adhesive joints by strength measurements was utilized in the study. The adhesive strength was determined by utilizing the single-lap shear test

[Mohan, 1990; Arnold, 1989; Tsai and Morton, 1994; ASTM, 1992]. The single-lap joint configuration (Figure 1) is widely used in the aerospace, automotive, and wood and plastic industries [Hermansen and Tunick, 1989; Arnold, 1989; Stringer, 1985; De Wilde, et al., 1995; Jialanella and Shaffer, 1993]. Single-lap specimens are economical, practical, and easy to make.

The durability of the adhesively bonded metal joints was investigated by measuring the joint strength before and after environmental exposure [Hermansen and Tunick, 1989].

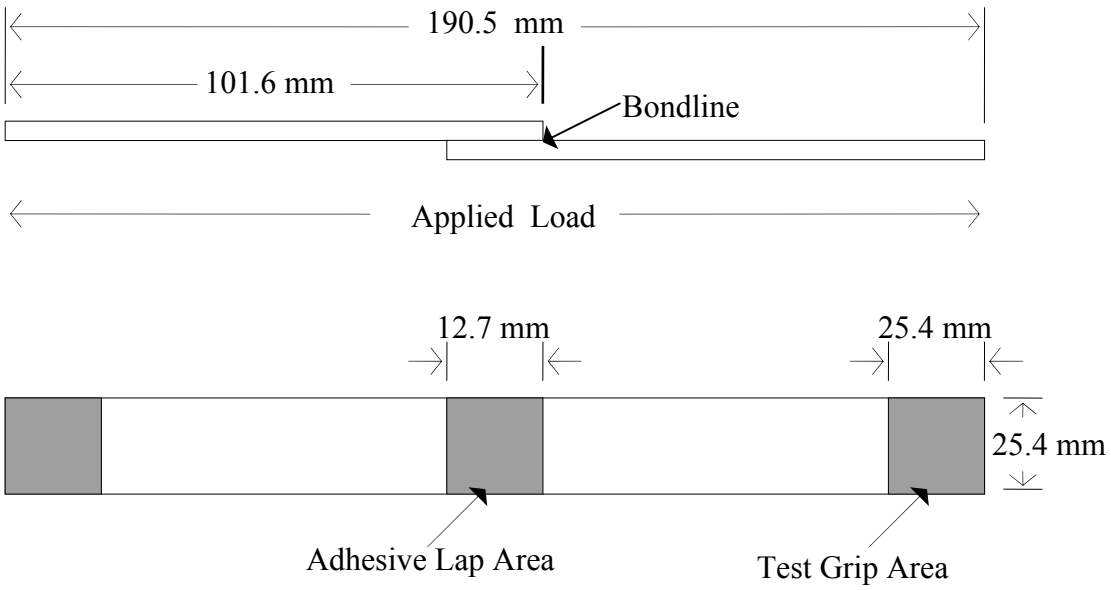


Figure 1. Single-lap shear joint configuration [Al-Harthi, 2003].

3.2 MATERIALS

The base epoxy adhesive used in this investigation is a general-purpose, two-part epoxy (Lord 309-1D epoxy resin and Lord 309-2D amine hardener) obtained from Lord Corporation, England. The adhesive is prepared by mixing equal volumes of the resin and hardener parts. The mixed adhesive cures fully in 24-48 hours at room temperature with handling strength in about 8 hours.

Rubber inclusion in the base epoxy is performed by mixing pre-determined amounts of the base epoxy resin and rubber modified epoxy resin RA-840 (obtained from CVC Specialty Chemicals, Maple Shade, USA) prior to curing. RA-840 (i.e. diglycidyl ether of bisphenol A modified with a CTBN elastomer) is a "pre-react"/ adduct where the CTBN rubber is reacted with excess epoxy to form a reactive epoxide with a CTBN backbone (it has an "epoxide equivalent weight" (EEW) of about 343 g/equiv. Its rubber content is 40 wt%. It has been reported that optimal toughening is achieved with use of about 10 parts rubber per 100 parts epoxy resin (about 9 wt% rubber) [Farris, 2002; Zarnitz, 2004] which corresponds to about 3.4 parts of Lord 309-1D resin (epoxy type A, with no rubber) and 1 part of RA-840 resin (epoxy type B, with 40% rubber). The amount of amine hardener (Lord 309-2D) to be added to cure RA-840 was determined to be about 0.7 part for each part of RA-840 by using different combinations and analyzing the physical and mechanical performance of the cured adhesive (theoretical determination was not possible since the "amine hydrogen equivalent weight" (AHEW) of the hardener was not known).

The aluminum powder used for filling the epoxy adhesive was obtained from Allied Britannia Limited. The aluminum particles are spherical/roundish with size smaller than 50 μm in diameter, as also seen in the SEM micrograph in Figure 2.

The aluminum sheets used as adherends in making aluminum joints are cut from locally obtained aluminum plates.

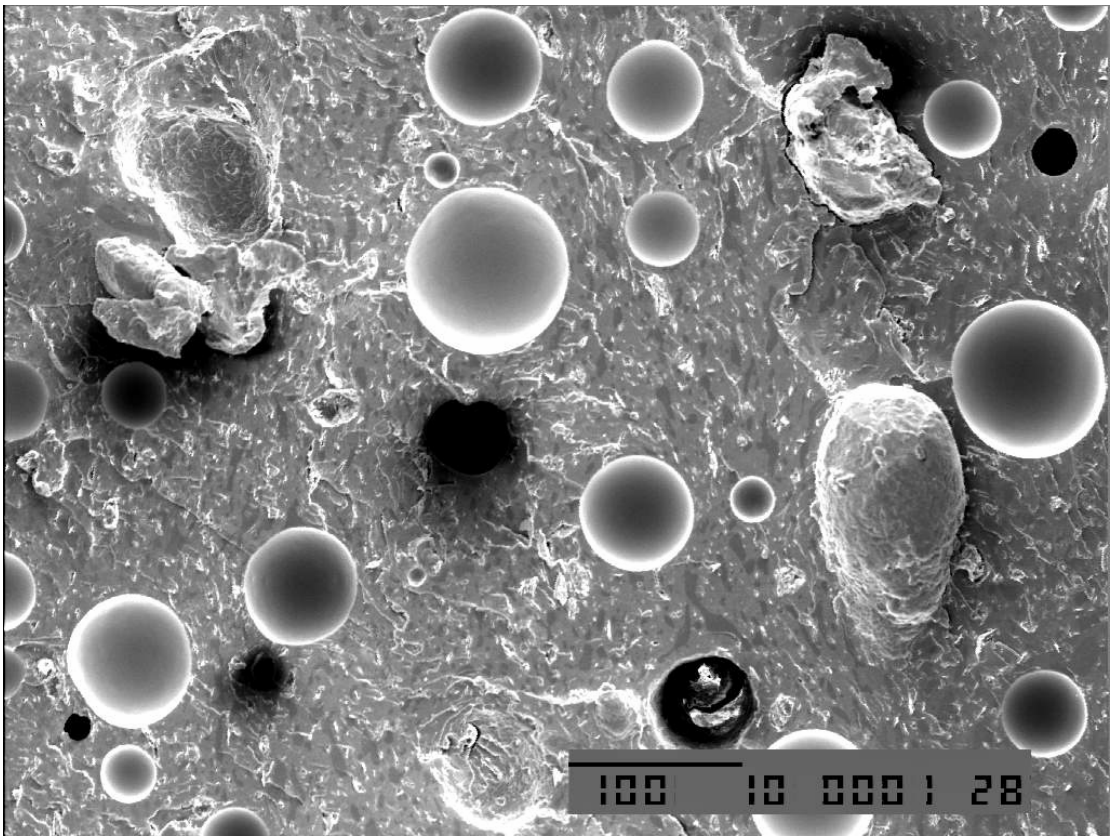


Figure 2. An SEM micrograph taken on a fractured cross-section of a cured aluminum filled epoxy adhesive [Al-Harthi, 2003].

3.3 MOISTURE DIFFUSION TESTS

The adhesive sheets (30.0×30.0×1.0 mm^3) for the moisture diffusion tests were molded between wax covered metal sheets. The details of the molding procedure are given in Appendix A.

Five different aluminum-rubber filler contents were studied as listed below:

1. 100% Epoxy (1 Part Lord 309-1D + 1 Part Lord 309-2D)
2. Epoxy with 25 wt% Al (25% Al + 75% {1 Part Lord 309-1D + 1 Part Lord 309-2D})
3. Epoxy with 40 wt% Rubber (1 Part RA-840 + 0.7 Part Lord 309-2D)
4. Epoxy with 9 wt% Rubber (3.4 Part Lord 309-1D + 1 Part RA-840 + 4.1 Part Lord 309-2D)
5. Epoxy with 25 wt% Al + 9 wt% Rubber (25% Al + 75% {3.4 Part Lord 309-1D + 1 Part RA-840 + 4.1 Part Lord 309-2D})

Three pieces of each particular adhesive were immersed in a solution for several months at room temperature. Five test solutions were utilized in the investigation: (1) distilled water; (2) 100 ppm sodium chloride solution; (3) 1000 ppm sodium chloride solution; (4) 0.5 M sodium chloride solution; (5) 1.0 M sodium chloride solution.

All test specimens were suspended/immersed in the test solutions without making contact with each other as shown Figure 3. The test solutions were covered with aluminum foil to prevent moisture evaporation. At various time intervals, test specimens were removed from the solution, dried with clean tissue and weighed by an analytical balance with precision to 0.0001 g.

Figure 3. A photograph of the adhesive specimens immersed in moisture diffusion test solutions [Al-Harthi, 2003].

3.4 ADHESIVE JOINT PREPARATION

The procedure given in Appendix B [Semerdjiev, 1970; Kozma and Olefjord, 1987; Prakash, et al., 1987; Al-Harthi, 2003] was used for cleaning the aluminum sheets (101.6×25.4×2.0 mm^3) before adhesively joining them.

The single-lap adhesive joints (as shown in Figure 4) were prepared by bonding surface cleaned/treated aluminum sheets together with the epoxy adhesive after addition of rubber and aluminum filler at fractions listed below:

1. Epoxy with 25 wt% Al (25% Al + 75% {1 Part Lord 309-1D + 1 Part Lord 309-2D})
2. Epoxy with 9 wt% Rubber (3.4 Part Lord 309-1D + 1 Part RA-840 + 4.1 Part Lord 309-2D)
3. Epoxy with 25 wt% Al + 9 wt% Rubber (25% Al + 75% {3.4 Part Lord 309-1D + 1 Part RA-840 + 4.1 Part Lord 309-2D})

Figure 4. A sample single lap specimen [Al-Harthi, 2003].

3.5 MECHANICAL CHARACTERIZATION OF THE ADHESIVE JOINTS

The adhesive joints were assembled and tested as specified in ASTM D 1002 [ASTM, 1992]. The joint configuration and the direction of the applied load are shown in Figure 1. End tabs of the same thickness and material of the adherends were used to place the load axis in the same plane of the overlap area. The equipment used for mechanical characterization was an Instron 5567 mechanical testing system as shown in Figure 5. Joint strengths, reported in units of shear stress, were calculated as follows:

$$Joint\ Strength = \frac{Failure\ Load}{Adhesive\ Lap\ Area} \tag{25}$$

Since the mechanical testing of adhesive joints usually yields scattered data, three specimens were prepared and tested and the results averaged, to achieve a reliable representation of adhesive joint performance, for each set of filler content and type and duration of the environmental exposure.

Figure 5. A photograph of the mechanical testing system [Al-Harthi, 2003].

3.6 ENVIRONMENTAL EXPOSURE OF THE ADHESIVE JOINTS

The adhesive joints were exposed for several periods of time to aggressive and corrosive environments such as those existing in Saudi Arabia weather of which can be characterized by high temperatures, high temperature variations from day to night, and salty and highly humid atmosphere in coastal regions. Two main types of environment were utilized for the weathering studies as listed in the details given below. The performance of the exposed adhesive joints were determined as described in Section 3.5 and compared to that of the control (unexposed) specimens.

3.6.1 Exposure to Test Solutions

Two test solutions were used in the investigation: (1) distilled water and (2) sea water. The adhesive joints were suspended/immersed in the test solutions as shown in Figure 6. At various time intervals, test specimens were removed from the solution for mechanical characterization.

3.6.2 Exposure to Saudi Arabian Atmosphere

The adhesive joints were mounted on the exposure racks located at Dhahran site for several durations of time ranging from one month to 10 months (Figure 7). At the end of their exposure period, the specimens were removed from the exposure racks for mechanical characterization.

Figure 6. Single-lap adhesive joints exposed in distilled water and seawater [Al-Harthi, 2003].

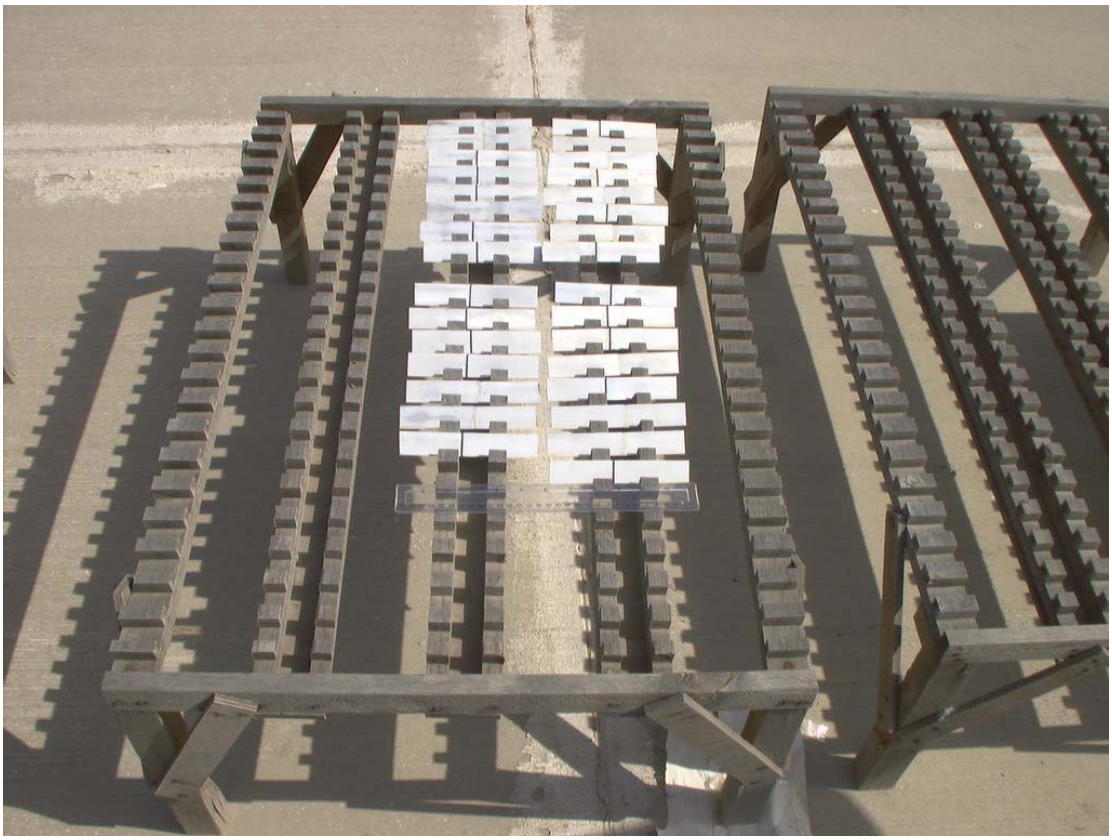


Figure 7. Single-lap adhesive joints exposed to atmosphere [Al-Harthi, 2003].

4. RESULTS AND DISSCUSSION

4.1 Moisture Diffusion Study

Moisture diffusion experiments lasted about 12 months in which diffusion in almost all the test specimens reached equilibrium. Plots of moisture uptake vs. immersion time in various solutions for epoxy adhesive specimens with five different filler contents (25 wt% Al, 25 wt% Al + 9 wt% rubber, 9 wt% rubber, 40 wt% rubber, no filler) are presented in Figures 8-17.

Diffusion curves in Figures 8-12 show that the adhesives in general absorb a larger amount of water upon exposure to distilled water or lightly concentrated salt solutions (100 ppm and 1000 ppm) than when exposed to highly concentrated salt solutions (0.5 M and 1.0 M). This situation has also been observed and discussed by Al-Harthi in his M.S. thesis (2003). This situation was explained by the reverse osmosis mechanism [Al-Harthi, 2003; Tai and Szklarska-Smialowska, 1993a]. When water is absorbed by the adhesive from the bulk solution, an electrolyte is produced upon dissolution of the internal water-soluble substances (inorganic fillers). Because of osmosis, water from the bulk solution is driven into the adhesive matrix to dilute the electrolyte. However, in the cases where the bulk sodium chloride solution is more concentrated than the electrolyte produced inside the adhesive matrix reverse osmosis occurs. The absorbed water is driven out of the adhesive matrix during reverse osmosis, therefore balancing the concentration difference between the internal electrolyte and the bulk NaCl solution. As a result the amount of water absorbed in the adhesive decreases with the concentration of the bulk NaCl solution. The only exception to this situation was the diffusion in the cured rubber modified epoxy RA-840 (epoxy type B) (Figure 12) which probably does not contain water-soluble contents at a significant level.

Figures 13-17 present plots of diffusant uptake vs. immersion time in each of the five test solutions for the adhesives with five different filler contents. In lightly concentrated salt solutions (Figure 13-15) epoxy type A (Lord 309 epoxy with no rubber content) absorbs larger amount of moisture than epoxy type B (rubber modified epoxy RA-840). However, as the salt content of the solution increases the maximum amount of moisture absorbed by epoxy type A decreases as discussed above and becomes even less than that absorbed by epoxy type B (Figures 16 and 17).

In general, epoxy adhesive with 9 wt% rubber which is a mixture of both epoxy types (3.4 parts epoxy type A and 1 part epoxy type B) absorbs moisture at an amount which is between those absorbed by each epoxy type. On the other hand, as expected aluminum filler incorporation in epoxy adhesive decreases its diffiusant uptake by decreasing the available volume for moisture diffusion [Al-Harthi, 2003].

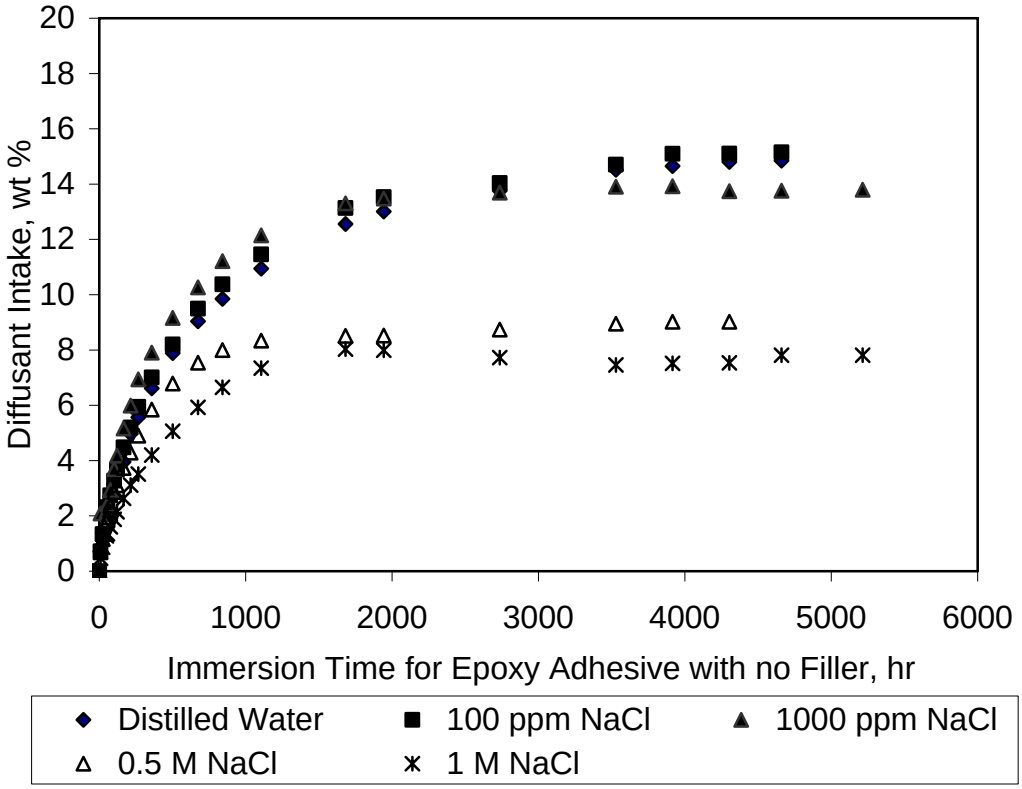


Figure 8. Diffusant intake (relative to the original weight of the specimen) vs. immersion time for epoxy adhesive with no filler in various test solutions.

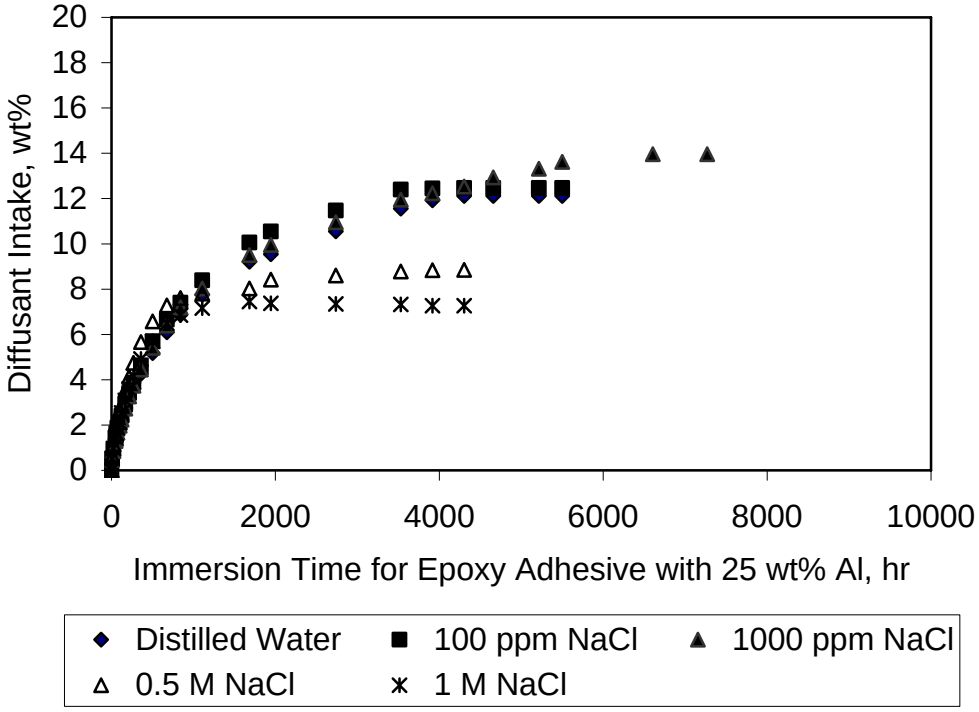


Figure 9. Diffusant intake (relative to the original weight of the specimen) vs. immersion time for epoxy adhesive with 25 wt% aluminum in various test solutions.

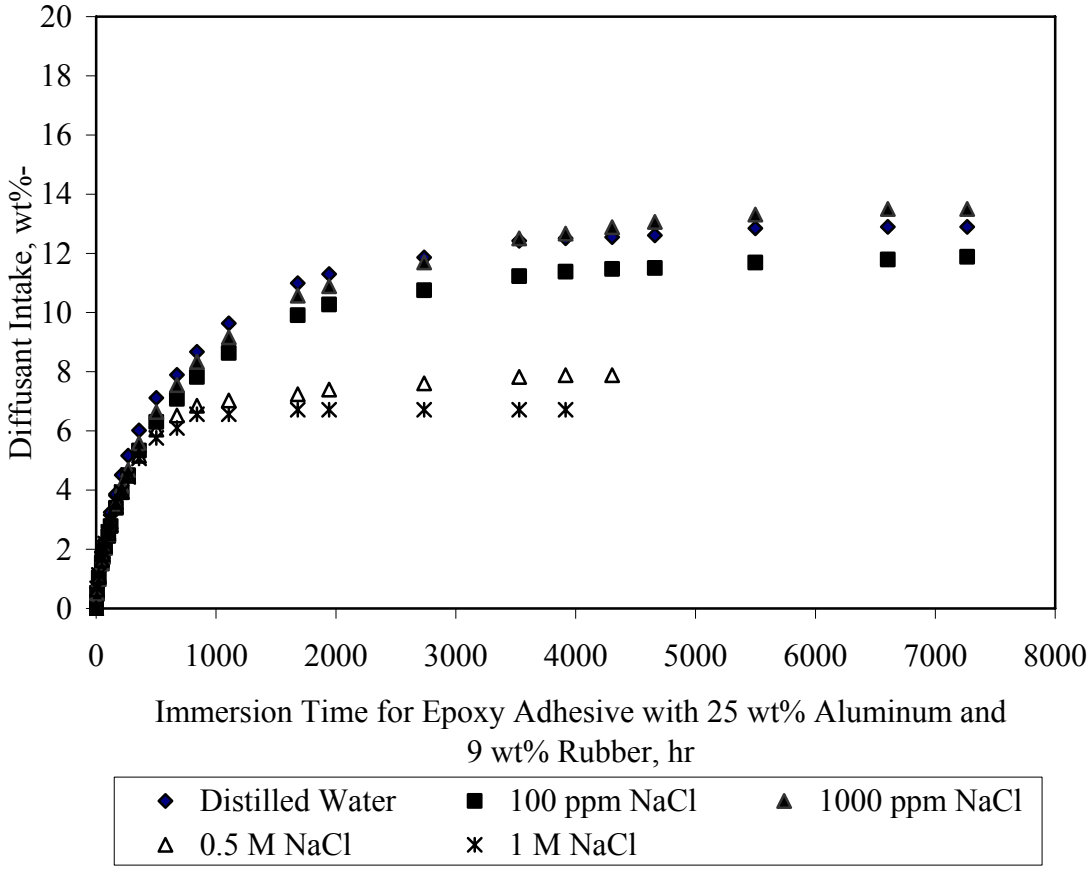


Figure 10. Diffusant intake (relative to the original weight of the specimen) vs. immersion time for epoxy adhesive with 25 wt% aluminum and 9 wt% rubber in various test solutions.

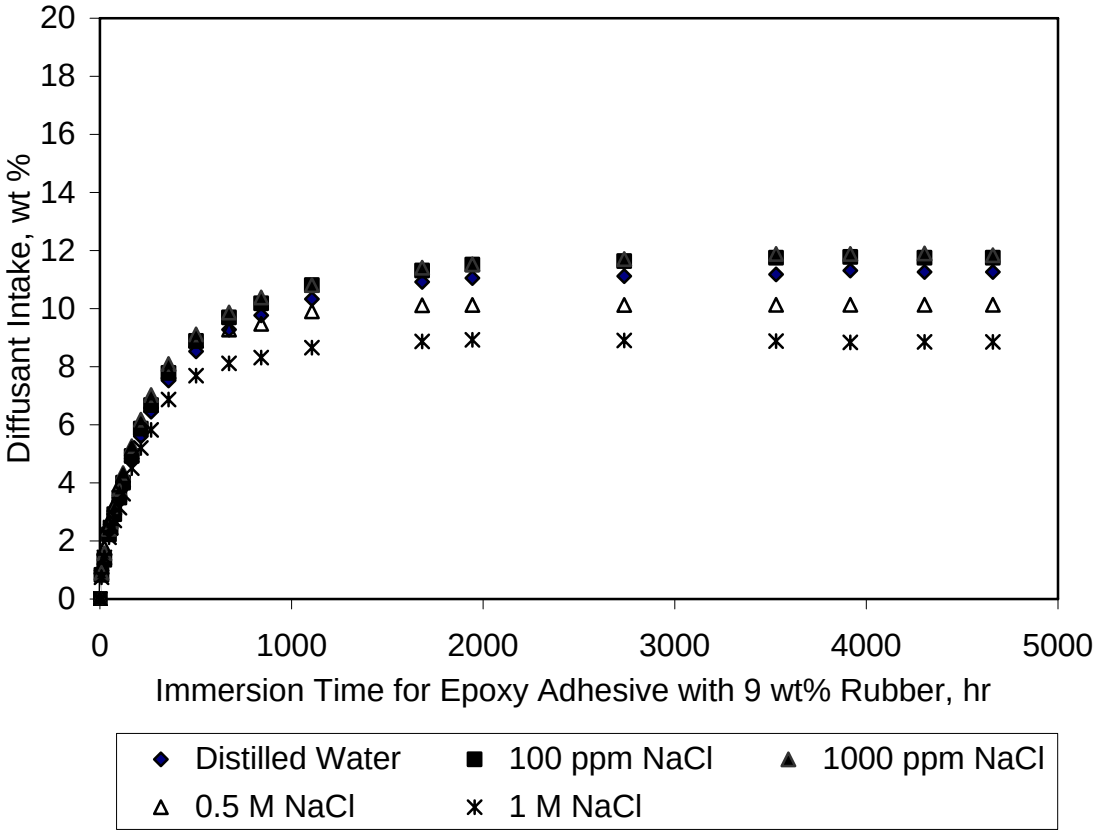


Figure 11. Diffusant intake (relative to the original weight of the specimen) vs. immersion time for epoxy adhesive with 9 wt% rubber in various test solutions.

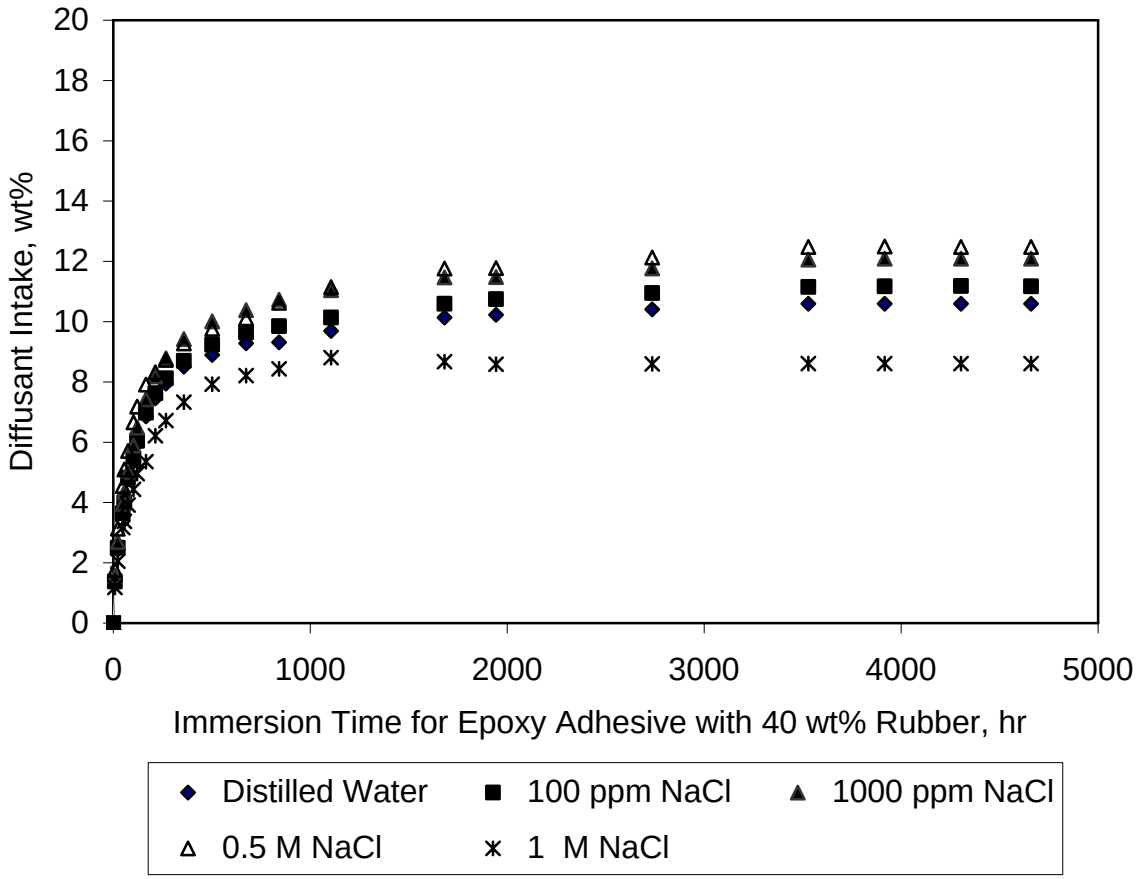


Figure 12. Diffusant intake (relative to the original weight of the specimen) vs. immersion time for epoxy adhesive with 40 wt% rubber in various test solutions.

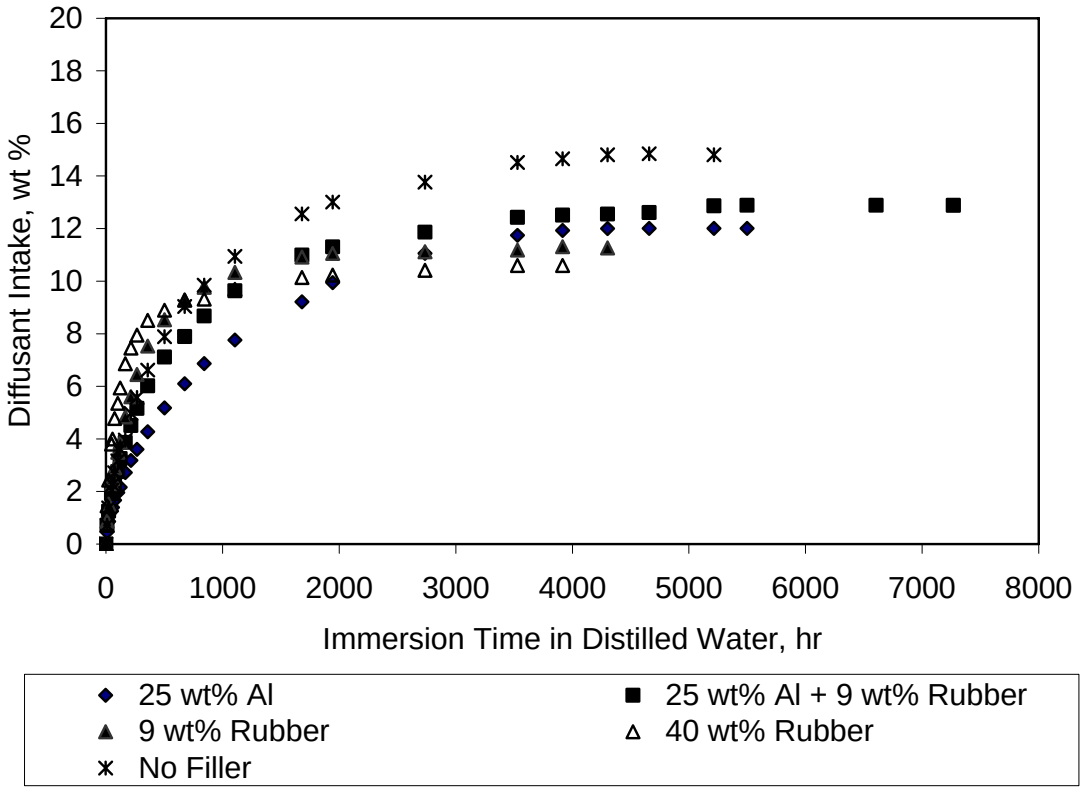


Figure 13. Diffusant intake (relative to the original weight of the specimen) vs. immersion time in distilled water for epoxy adhesive with five different filler contents.

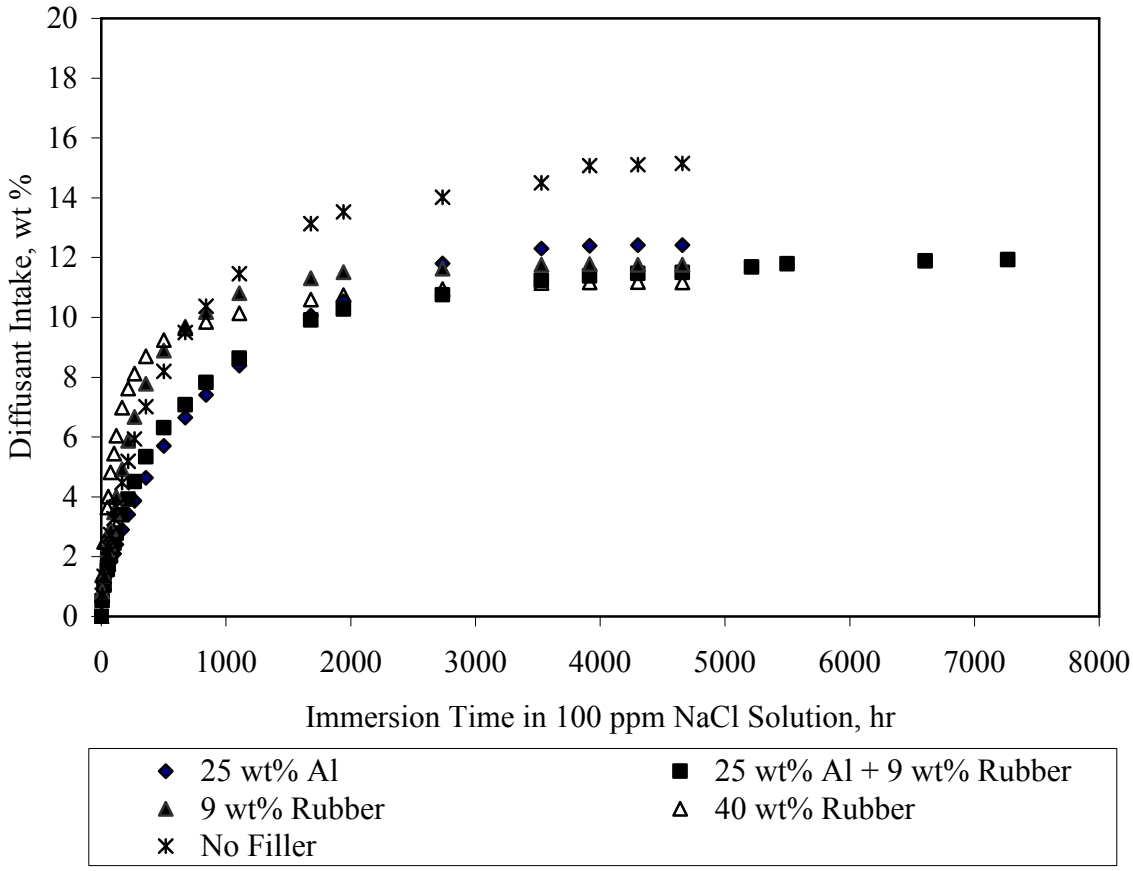


Figure 14. Diffusant intake (relative to the original weight of the specimen) vs. immersion time in 100 ppm NaCl solution for epoxy adhesive with five different filler contents.

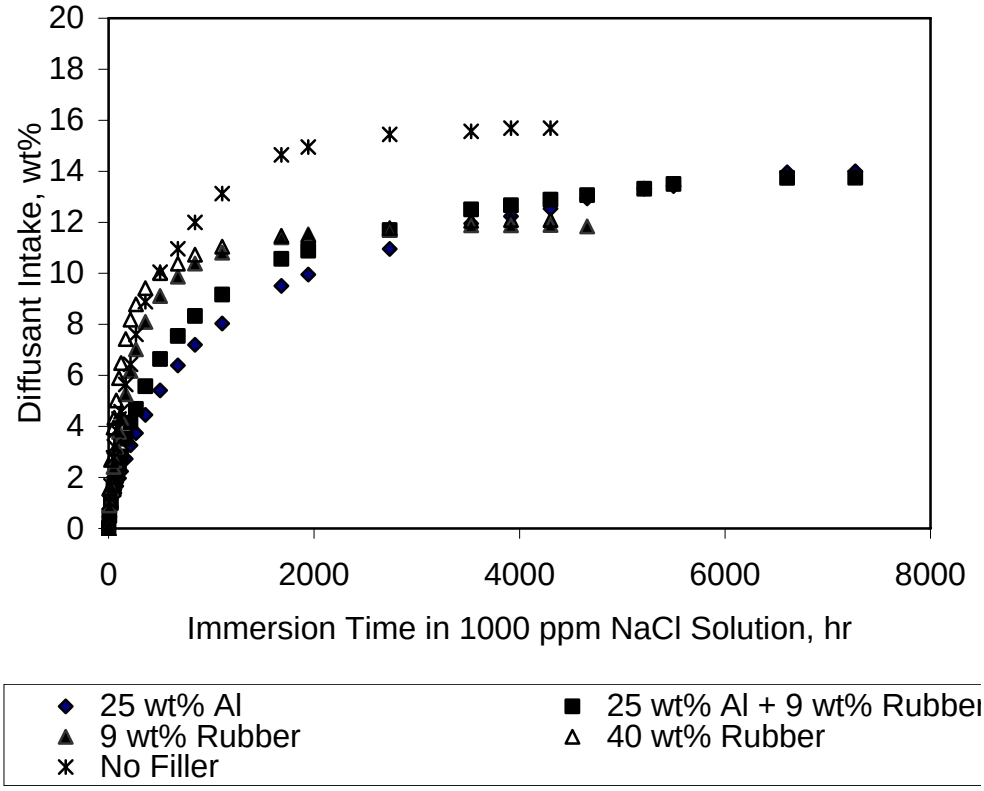


Figure 15. Diffusant intake (relative to the original weight of the specimen) vs. immersion time in 1000 ppm NaCl solution for epoxy adhesive with five different filler contents.

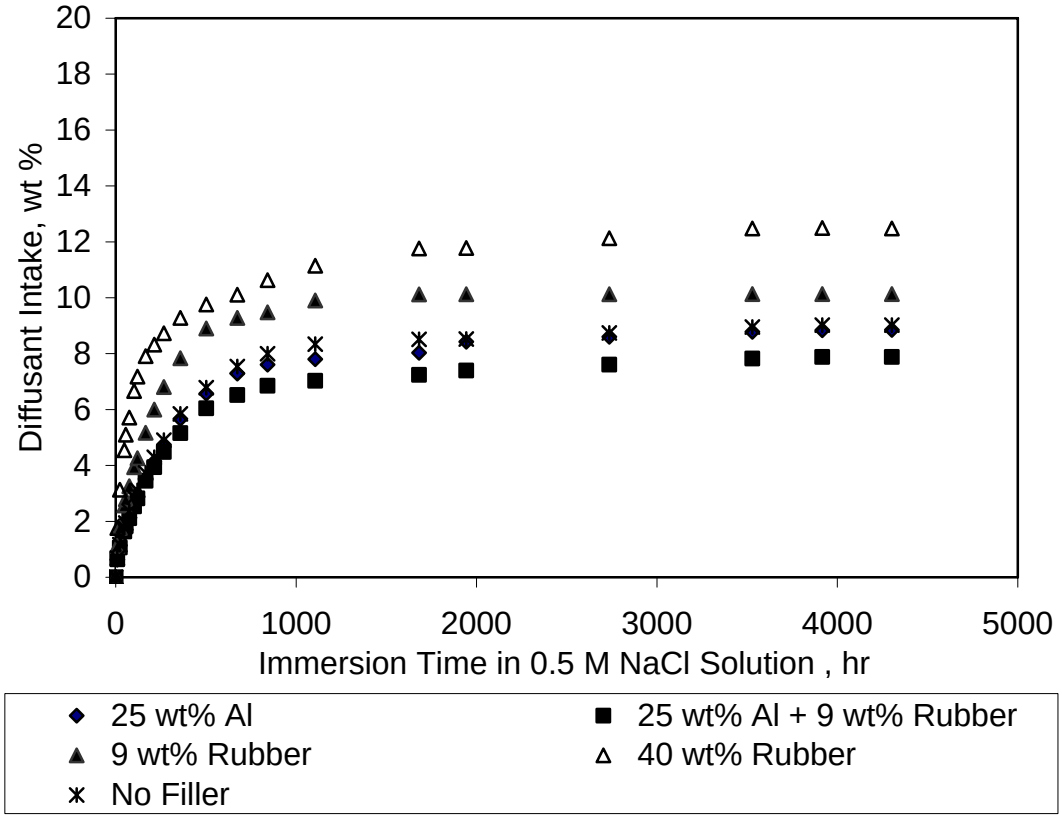


Figure 16. Diffusant intake (relative to the original weight of the specimen) vs. immersion time in 0.5 M NaCl solution for epoxy adhesive with five different filler contents.

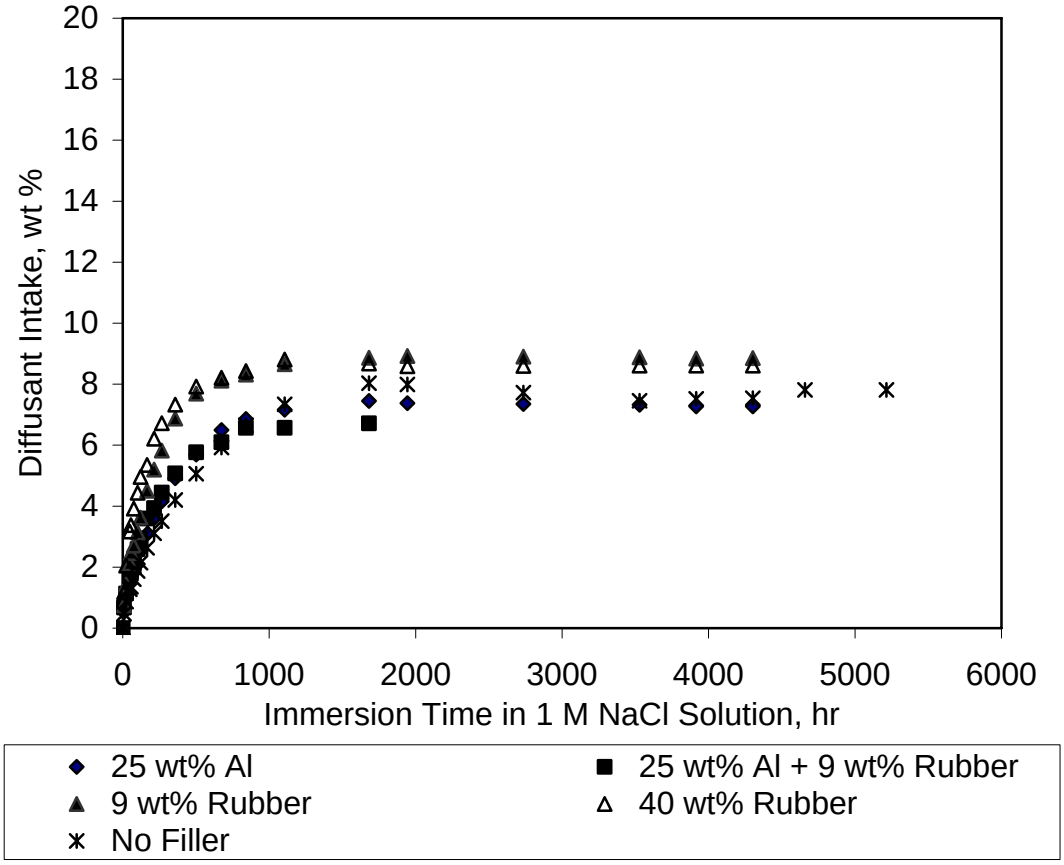


Figure 17. Diffusant intake (relative to the original weight of the specimen) vs. immersion time in 1 M NaCl solution for epoxy adhesive with five different filler contents.

Diffusivities of moisture in epoxy adhesive specimens with different filler contents in five test solutions were determined by use of Equations 20. In this method, fractional uptake (M_t/M_∞) is plotted against $4(t/\pi\ell^2)^{1/2}$ and the apparent diffusivity is determined from the initial slope of the plot (usually first four-five points) (slope is $D^{1/2}$). A representative plot is presented in Figure 18 (for epoxy adhesive (Type A) with no rubber or aluminum filler in 100 ppm NaCl solution). Apparent diffusivities determined are presented in Figures 19-28.

As shown in Figures 19-23, the rate of moisture diffusion is much faster in epoxy type B having 40 wt% rubber content (RA-840) than in epoxy type A (Lord 309) with no rubber or aluminum filler or with 25 wt% aluminum filler content. In general, aluminum filler content did not have a significant effect on moisture diffusivity, with some scattering in data. Moisture diffusivity in epoxy with 9 wt% rubber, which is a mixture of epoxy type A (with no rubber content) and epoxy type B (with 40 wt% rubber) was in between the diffusivities in each epoxy type.

The data were also plotted in a way to show the effect of solution salt concentration on moisture diffusivity in Figures 24-28 (as diffusivity vs. solution type for each adhesive content). As shown in the figures, the rate of diffusion is faster in the test solutions with high salt content (0.5 M and 1.0 M NaCl solutions) than in those with low salt content (distilled water, 100 ppm and 1000 ppm NaCl solutions) (Figures 24-27) except for the epoxy type B with 40 wt% rubber content for which no effect of salt concentration on diffusion rate was observed (Figure 28).

Tai and Szklarska-Smialowska (1993b) states that concentrated salt solutions somehow enhance the formation of microcavities in adhesive materials and this increases the rate of moisture diffusion. The above results show that this might be true for the

specimens containing epoxy type A (Load 309) but not for epoxy type B with 40 wt% rubber content (RA-840).

Diffusivities were also, determined by use of Equation 22 in which $\ln(1-M_t/M_\infty)$ is plotted against $\pi^2 t/\ell^2$ as in Figure C1 in Appendix C and the diffusivity is determined from the slope of the straight line at large times (ranges between -1 and -4 in the y-axis) (slope is $-D$). The results were very similar to the results presented above and are summarized in the plots in Figures C2-C11 in Appendix C. Diffusivity values obtained through both methods (by use of Equation 20 and 22) are also given in Tables D1-D5 in Appendix D.

Reliability of the experimental data was also checked by determining the fractional uptake (M_t/M_∞) as a function of time from the analytical relation (Equation 21) and comparing it with the experimental observation for each case. The theoretically and experimentally determined fractional uptake vs. time plots matched very well, as a sample is presented in Figure 29 for epoxy adhesive with no filler in 0.5 NaCl solution. Similar results were obtained for all other cases as well, which are presented in Appendix E. In these plots, the average diffusivity as determined from equations 20 and 22 presented in appendix D was used in the theoretical calculation.

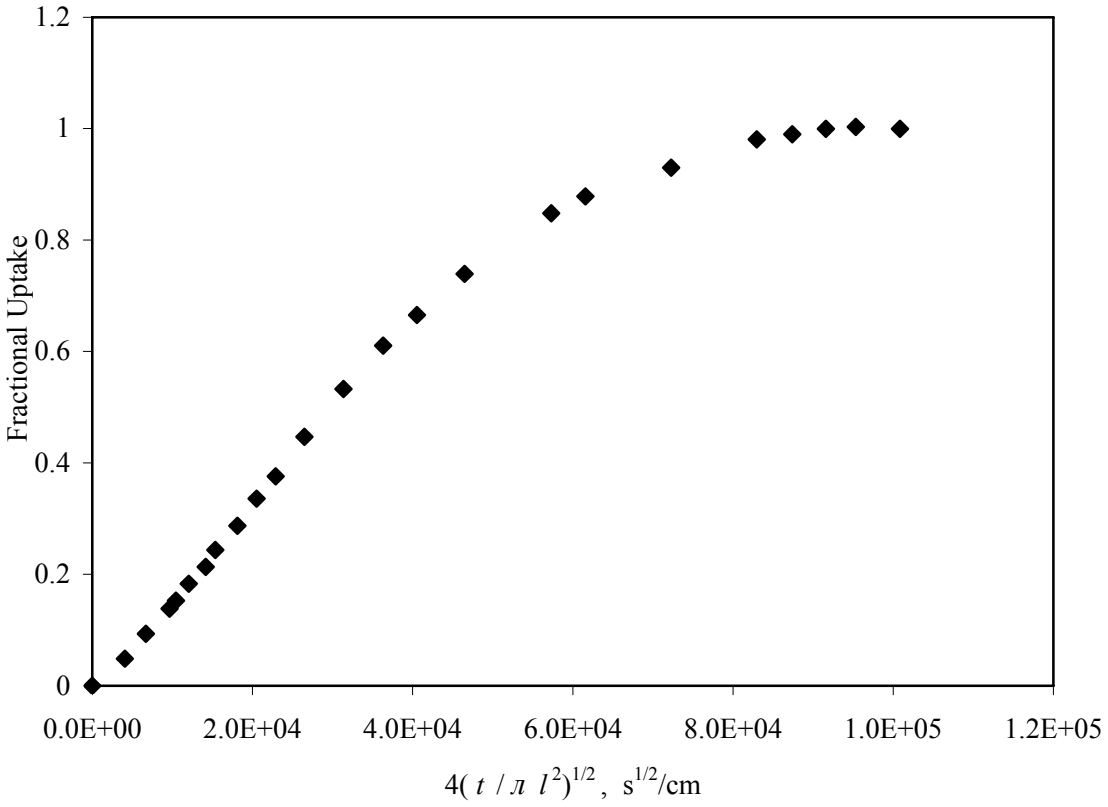


Figure 18. Representative plot of fractional uptake (M_t/M_∞) vs. $4(t/\pi l^2)^{1/2}$ for epoxy adhesive with no filler in 100 ppm NaCl.

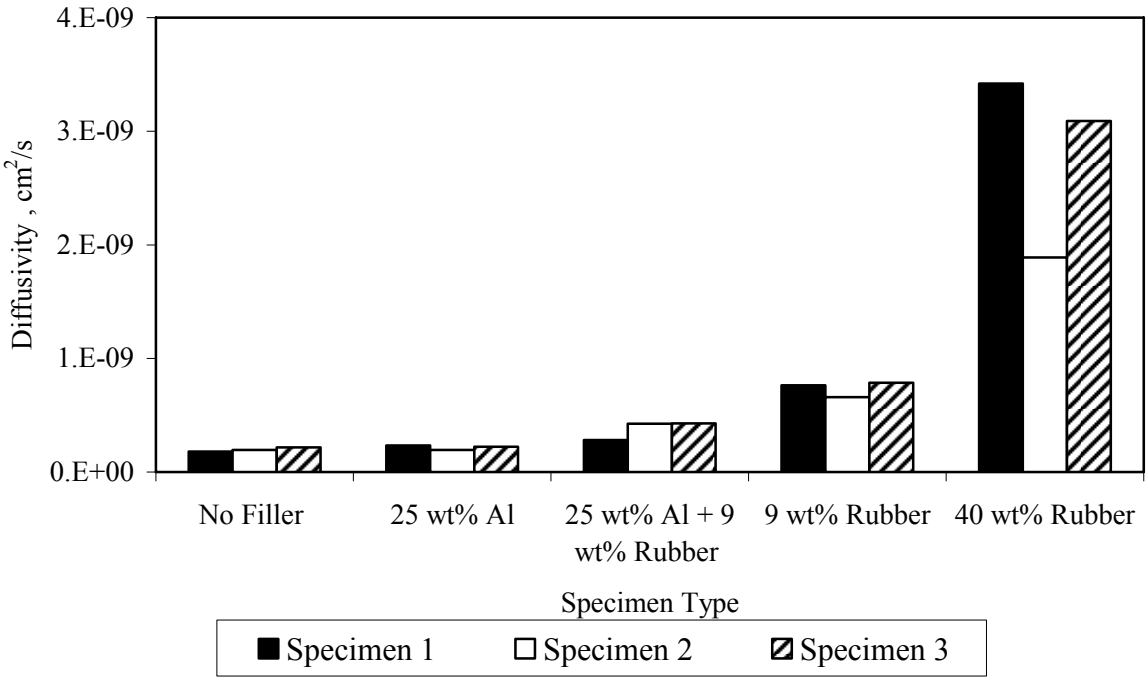


Figure 19. Diffusivity in distilled water vs. specimen type.

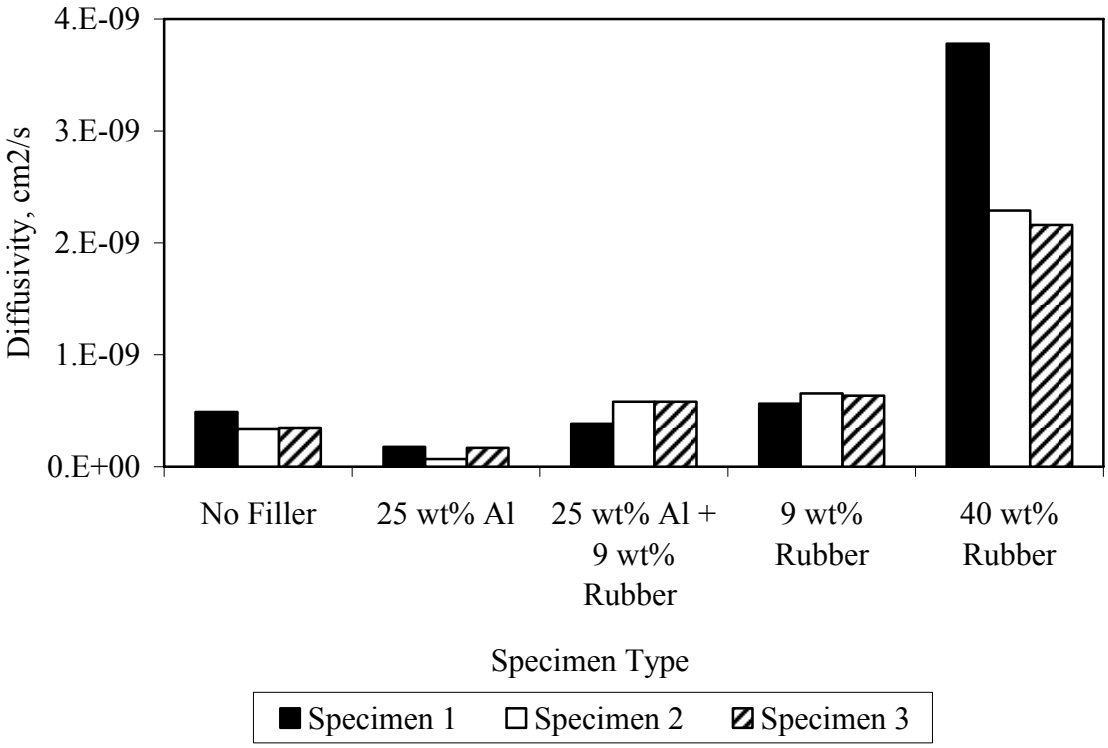


Figure 20. Diffusivity in 100 ppm NaCl solution vs. specimen type.

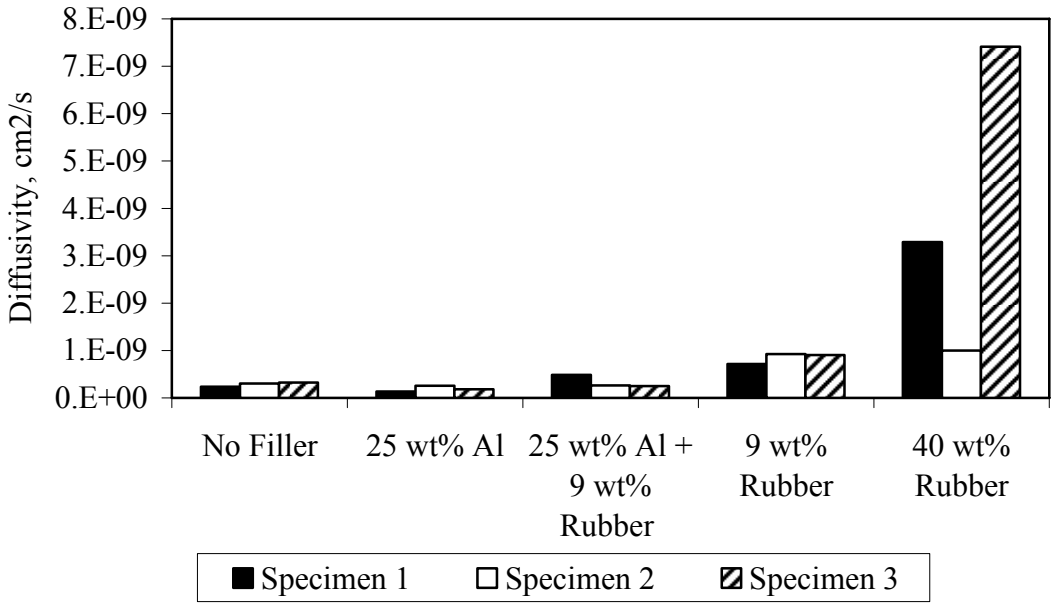


Figure 21. Diffusivity in 1000 ppm NaCl solution vs. specimen type.

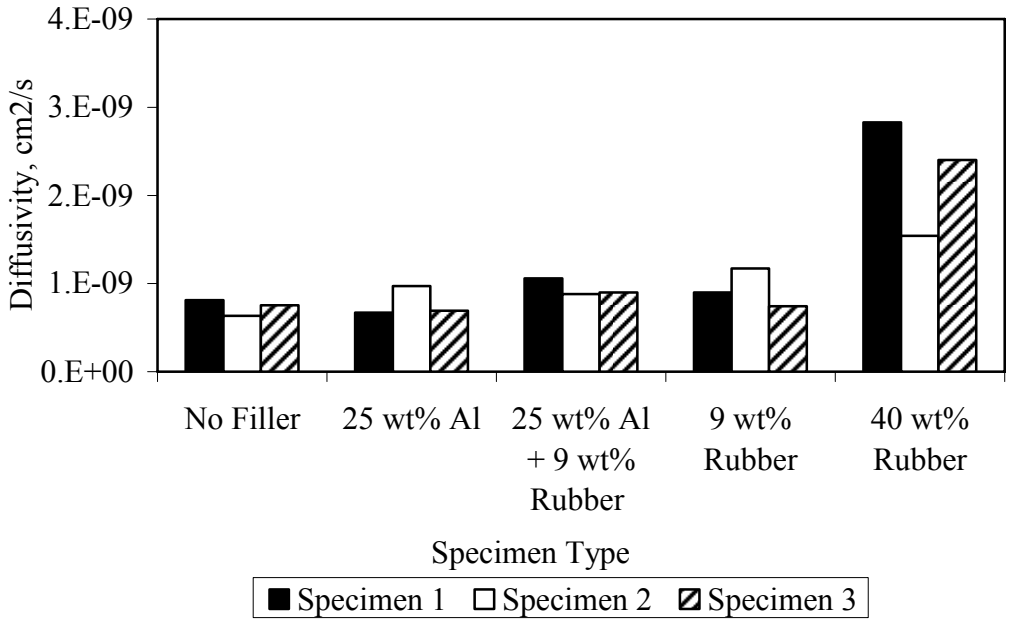


Figure 22. Diffusivity in 0.5 M NaCl solution vs. specimen type.

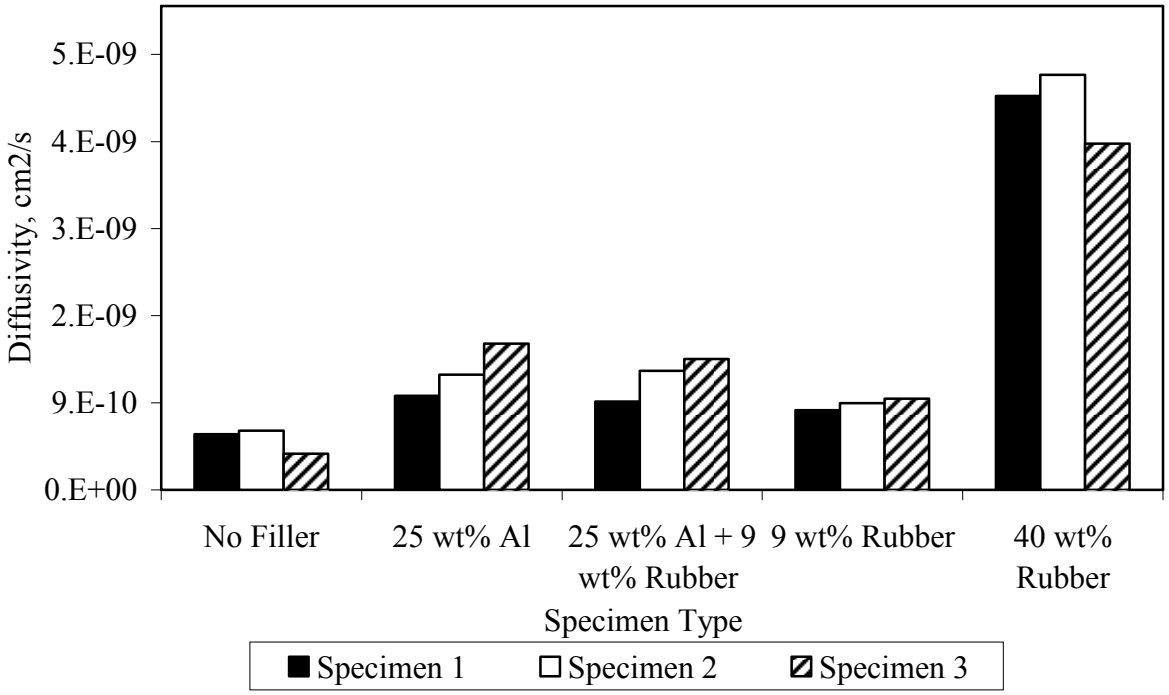


Figure 23. Diffusivity in 1.0 M NaCl solution vs. specimen type.

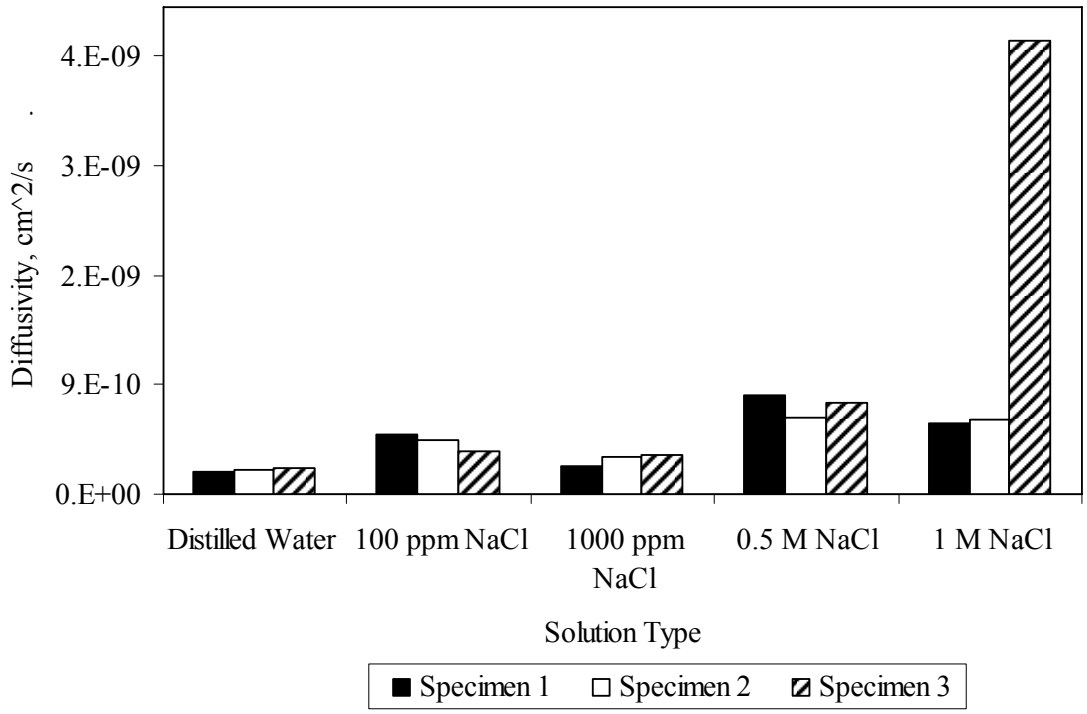


Figure 24. Diffusivity in epoxy adhesive with no filler vs. solution type.

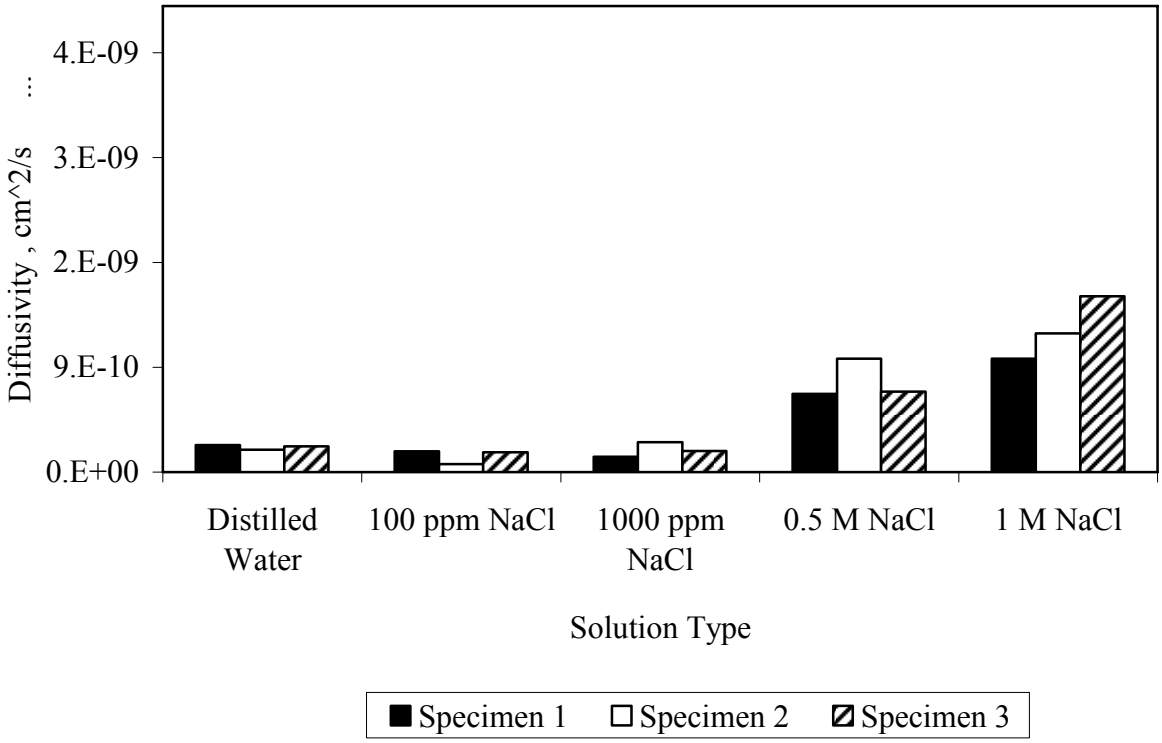


Figure 25. Diffusivity in epoxy adhesive with 25 wt% aluminum vs. solution type.

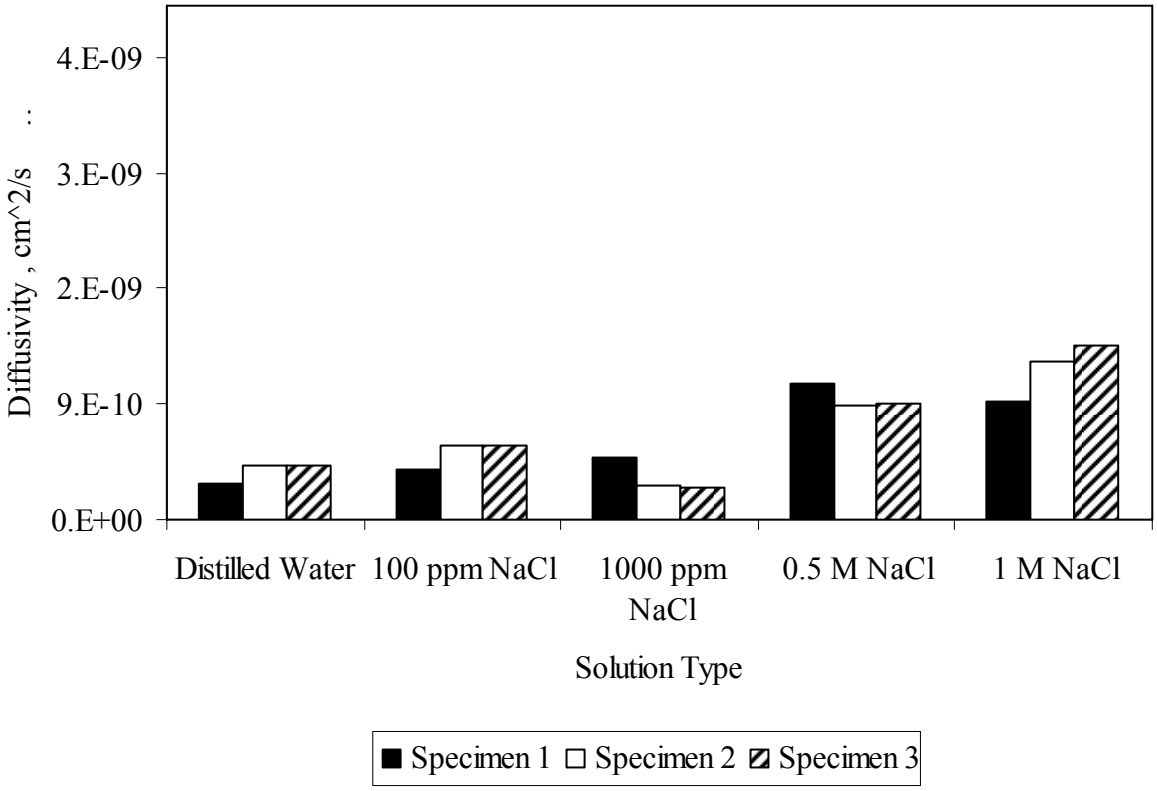


Figure 26. Diffusivity in epoxy adhesive with 9 wt% rubber and 25 wt% aluminum filler vs. solution type.

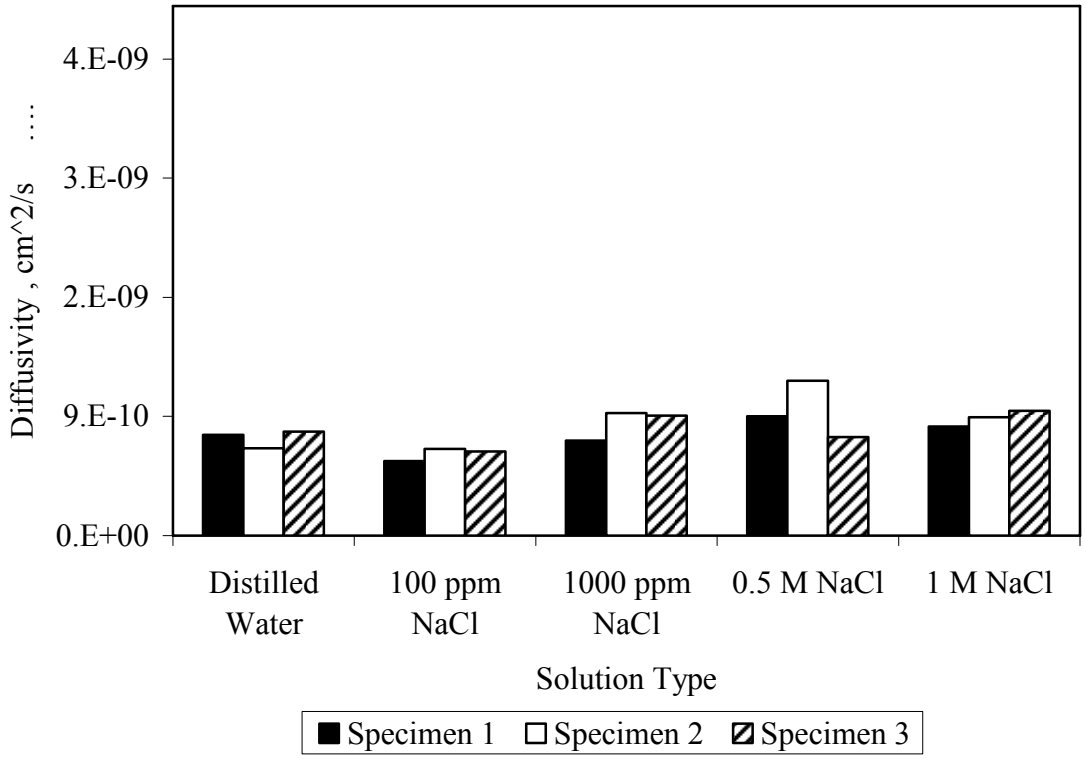


Figure 27. Diffusivity in epoxy adhesive with 9 wt% rubber vs. solution type.

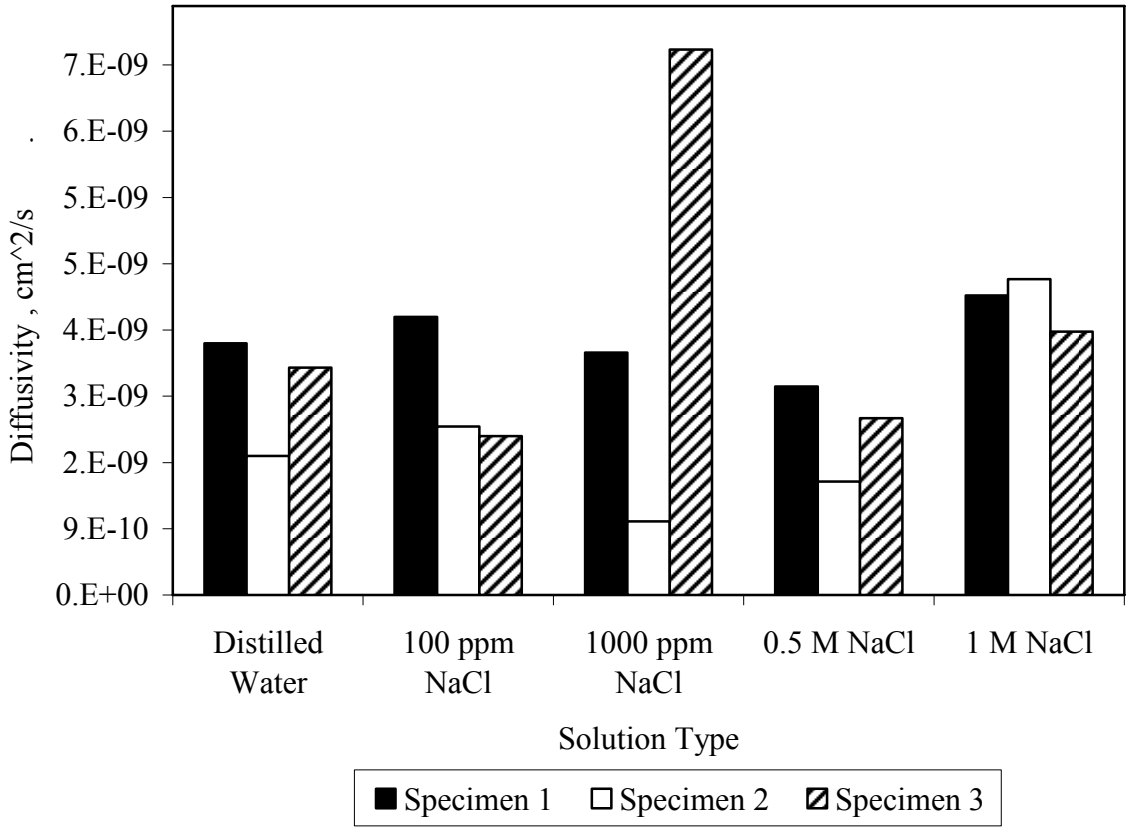


Figure 28. Diffusivity in epoxy adhesive with 40 wt% rubber vs. solution type.

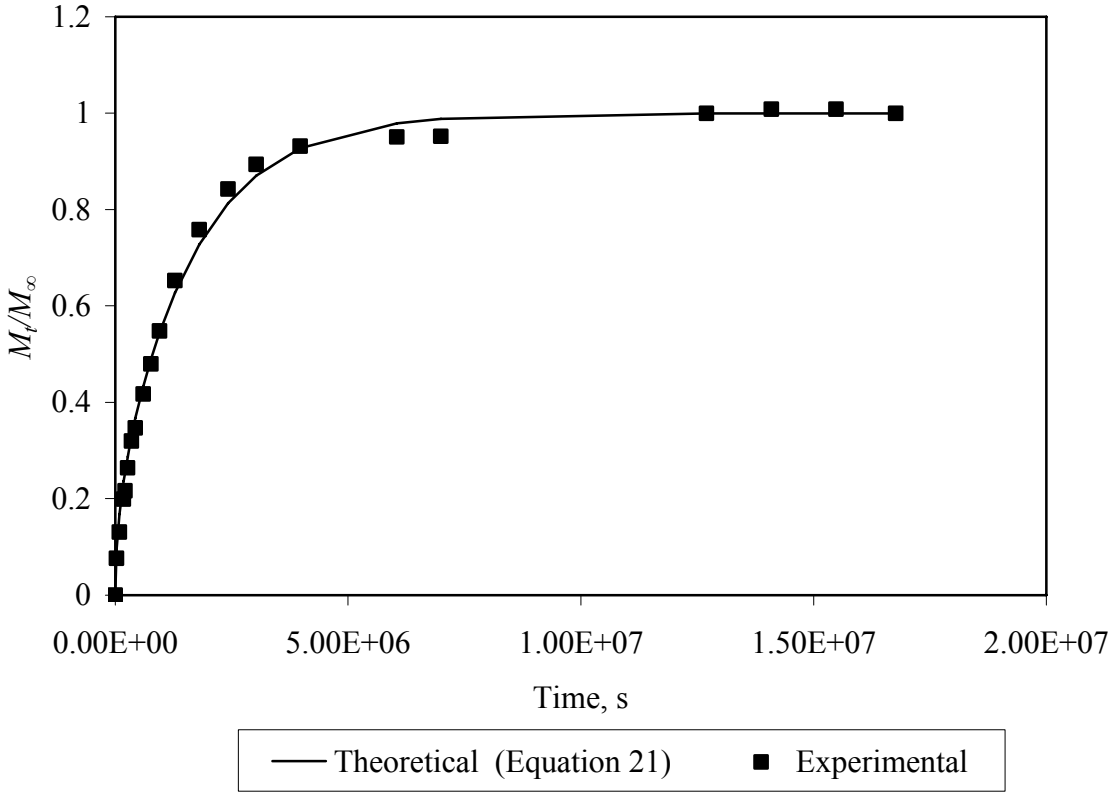


Figure 29. Theoretical and experimental fractional uptake vs. time for pure epoxy adhesive with no filler in 0.5 M NaCl solution.

4.2. Mechanical Characterization and Durability of Adhesive Joints

The single lap shear strengths of aluminum joints bonded with epoxy adhesive with various filler contents are presented in Figure 30. As the figure shows adhesion strength of the base epoxy with no filler content (epoxy type A) is similar to that of the rubber modified epoxy with 40 wt% rubber content (epoxy type B) (considering the scatter in data). Hence, inclusion of rubber in the base epoxy by mixing it with the rubber modified epoxy does not affect its adhesion strength negatively.

Figure 30 also shows a very promising result that varying the aluminum filler content in the adhesive from none to as much as 75 wt% did not have any decreasing effect on the adhesive strength. Based on these results inclusion of rubber and aluminum filler together in the adhesive would not affect the adhesion strength of the adhesive and it did not as also shown in Figure 30.

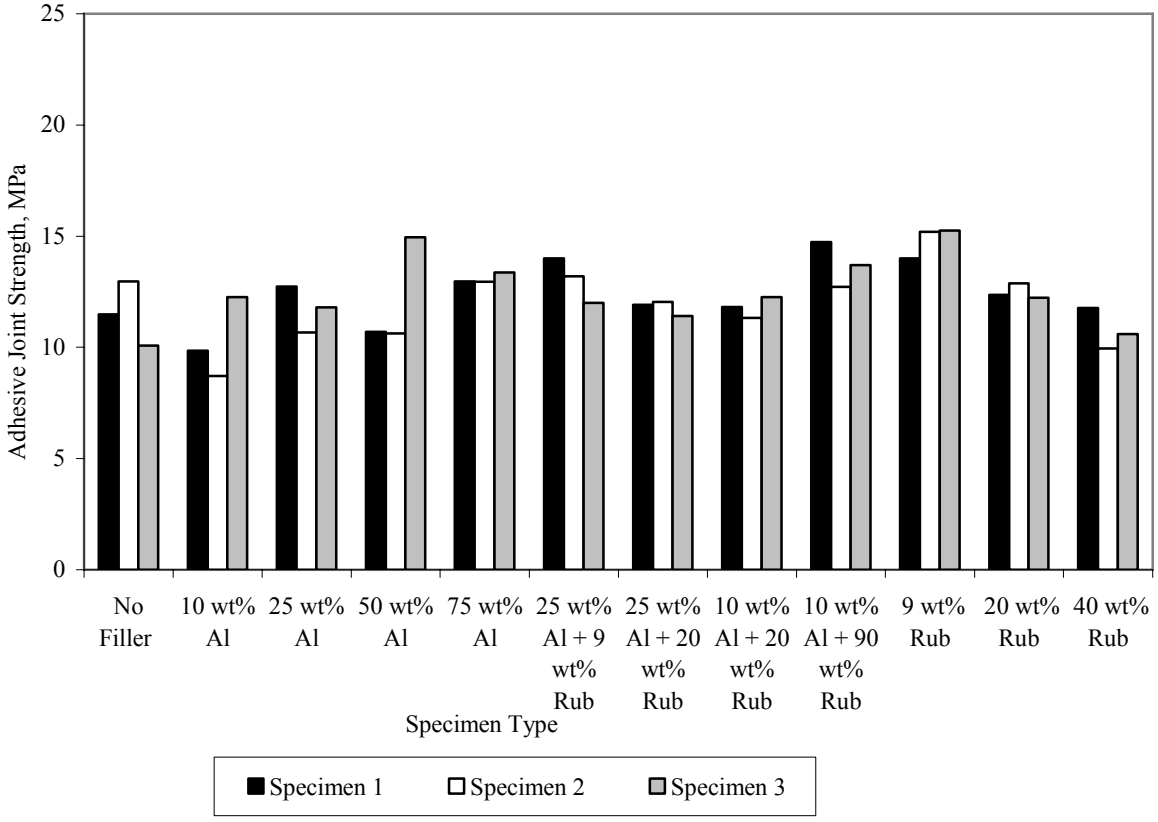


Figure 30. Adhesive joint strength vs. specimen type with no environmental exposure.

Figures 31-39 summarize the results of the environmental degradation experiments. Figures 31-33 plot adhesive joint strength of epoxy adhesive with 25 wt% aluminum filler vs. exposure time in atmosphere, distilled water and sea water, respectively. Figures 34-36 plot the same for epoxy adhesive with 9 wt% rubber and Figures 37-39 for epoxy adhesive with 9 wt% rubber and 25 wt% aluminum filler.

All the joints exposed to the hot and humid atmosphere of the Gulf kept their strength for as long as 10 months (Figures 31, 34 and 37). However, significant strength decrease was observed with exposure to distilled water (Figures 32, 35 and 38) or sea water (Figures 33, 36 and 39). In general, degradation started earlier in sea water than in distilled water which is consistent with higher diffusivity in concentrated salt solutions than in distilled water (based on the results of the diffusion study presented earlier). Levels of degradation in distilled water and sea water are, however, comparable at high exposure times inspite of more water absorbed in distilled water than in sea water in the case of the specimens examined as discussed earlier.

The effect of distilled water on adhesive degradation is more significant in the epoxy with 9 wt% rubber (Figure 35) than in the epoxy with no rubber content (Figure 32). This is consistent with higher diffusion rate in distilled water for rubber modified epoxy than for the base epoxy with no rubber content, eventhough rubber modified epoxy absorbs more water in distilled water at saturation than the base epoxy.

The effect of sea water on adhesive degradation was similar for the three types of the adhesives studied (Figure 33, 36 and 39). This is consistent with similar diffusivity values and similar maximum moisture intake values obtained for the adhesives immersed in sea water.

The effect of aluminum filler content on the environmental degradation of the adhesive strength was not examined here since it was studied earlier by Al-Harthi (2003) and concluded that aluminum filler content as much as 50 wt% does not have a significant effect on adhesive strength in environments such as the Gulf atmosphere, distilled water and sea water.

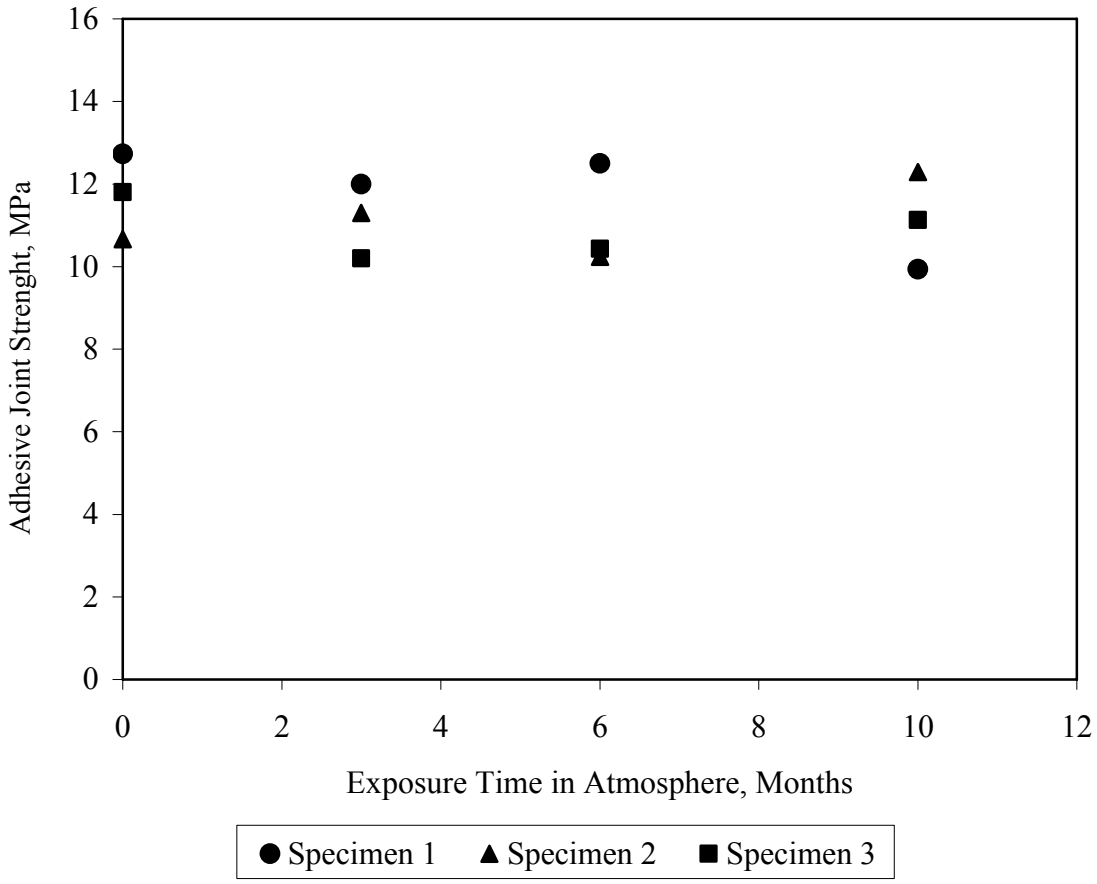


Figure 31. Adhesive joint strength of epoxy adhesive with 25 wt% aluminum filler vs. exposure time in atmosphere.

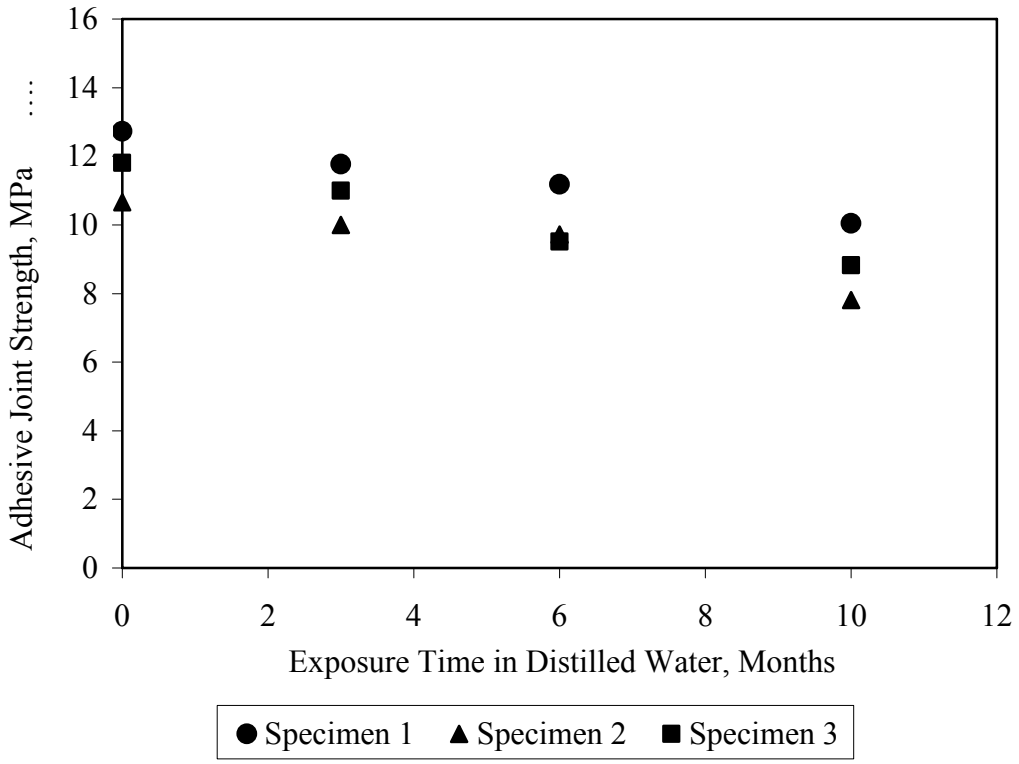


Figure 32. Adhesive joint strength of epoxy adhesive with 25 wt% aluminum filler vs. exposure time in distilled water.

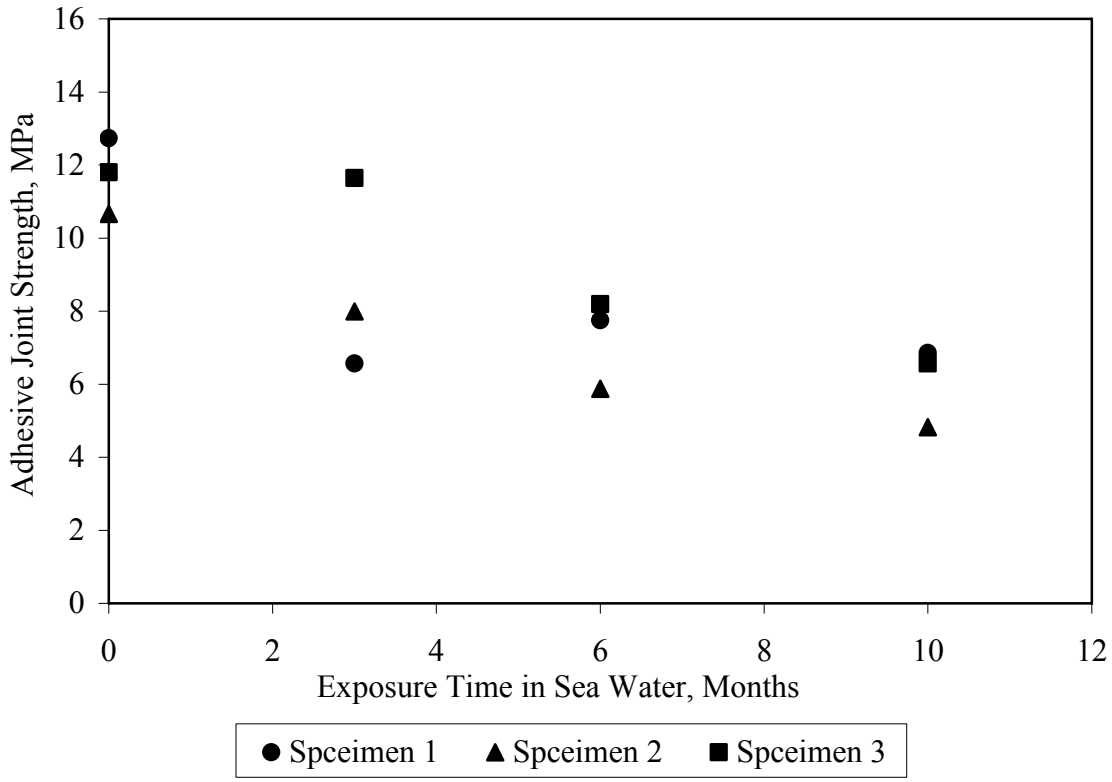


Figure 33. Adhesive joint strength of epoxy adhesive with 25 wt% aluminum filler vs. exposure time in sea water.

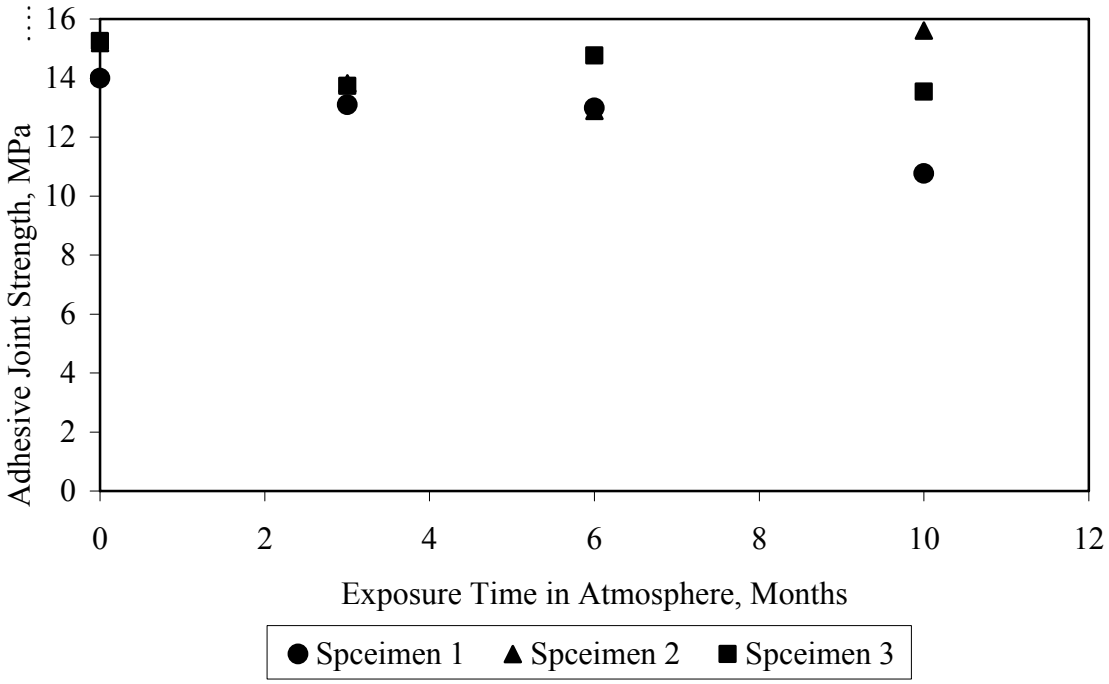


Figure 34. Adhesive joint strength of epoxy adhesive with 9 wt% rubber vs. exposure time in atmosphere.

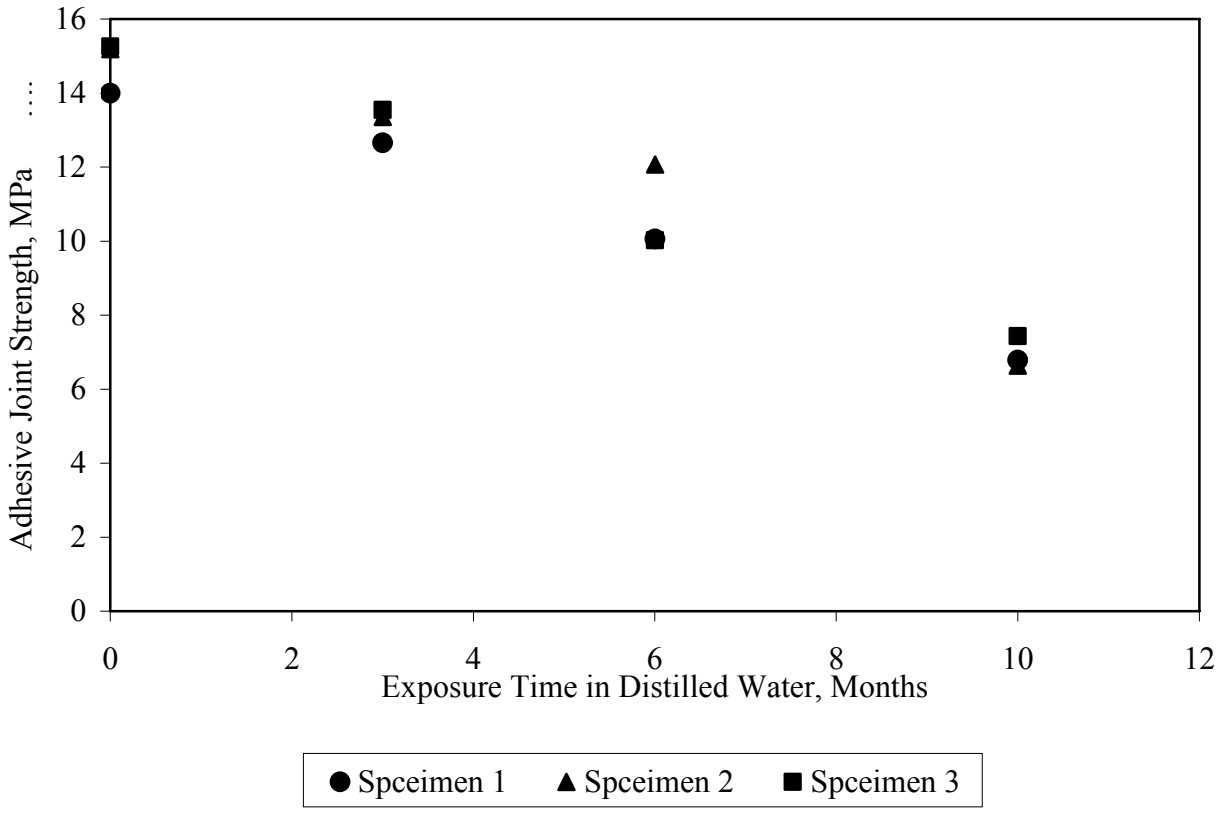


Figure 35. Adhesive joint strength of epoxy adhesive with 9 wt% rubber vs. exposure time in distilled water.

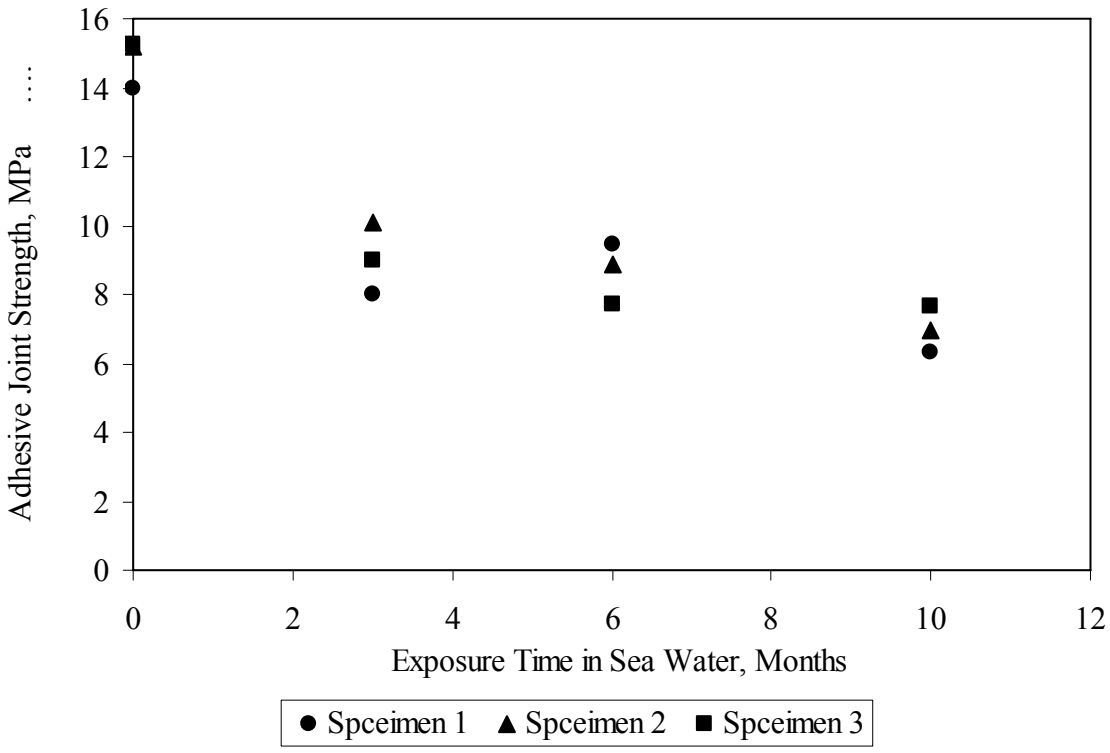


Figure 36. Adhesive joint strength of epoxy adhesive with 9 wt% rubber vs. exposure time in sea water.

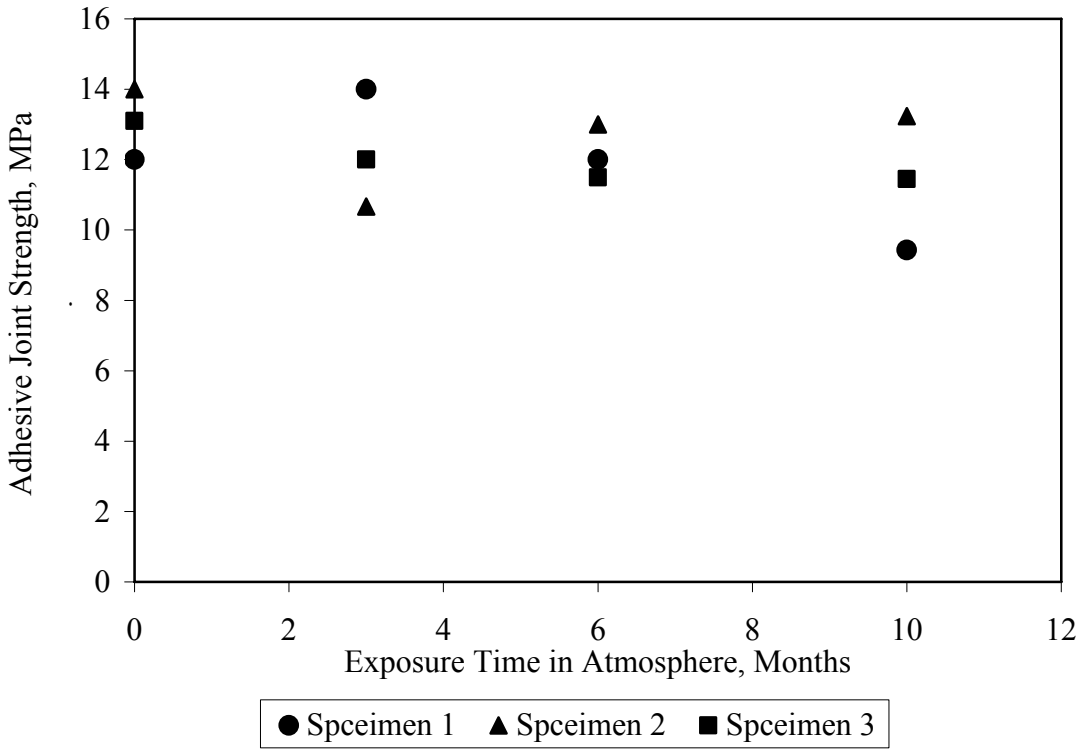


Figure 37. Adhesive joint strength of epoxy adhesive with 9 wt% rubber and 25 wt% aluminum filler vs. exposure time in atmosphere.

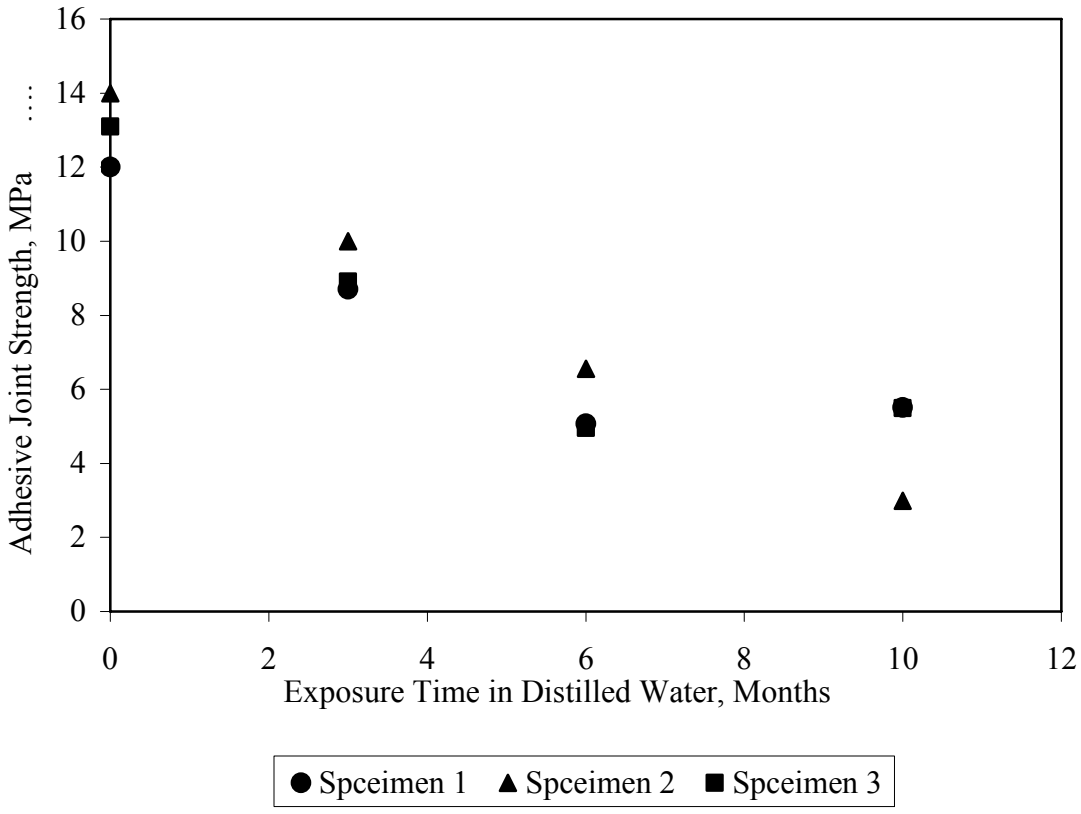


Figure 38. Adhesive joint strength of epoxy adhesive with 9 wt% rubber and 25 wt% aluminum filler vs. exposure time in distilled water.

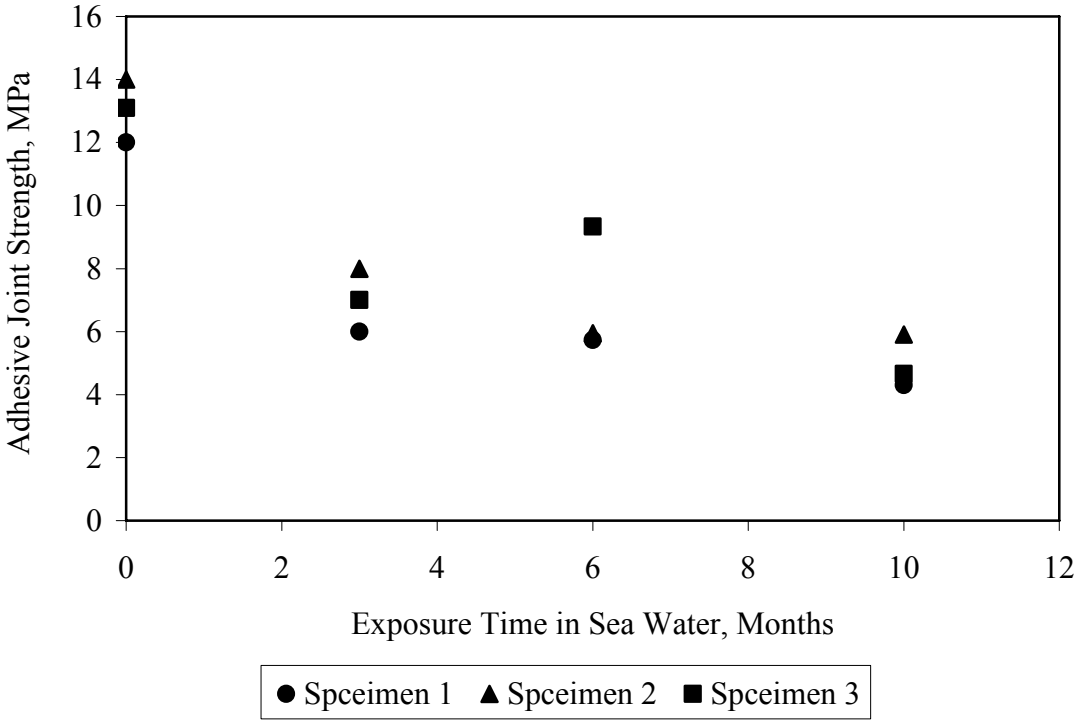


Figure 39. Adhesive joint strength of epoxy adhesive with 9 wt% rubber and 25 wt% aluminum filler vs. exposure time in sea water.

5. CONCLUSIONS

Epoxy type A with no rubber content (Lord 309) absorbs larger amount of moisture than epoxy type B with 40 wt% rubber content (RA-840) in distilled water and lightly concentrated salt solutions.

Maximum amount of moisture sorption into the adhesives containing epoxy type A decreases as the salt concentration of the exposure solution increases. However, there appears to be no significant effect of solution salt content on the maximum amount of moisture intake by the rubber modified epoxy RA-840 (at 40 wt% rubber content).

Decrease of moisture sorption amount in epoxy type A as the salt content of the solution increases results in lower moisture sorption in epoxy type A than epoxy type B in highly concentrated salt solutions.

Moisture diffusivity is higher in epoxy type B than epoxy type A in all five test solutions examined in this study. Moisture diffusivity in the adhesive increases as the rubber content of the adhesive increases by adding epoxy type B (with 40 wt% rubber content) to epoxy type A (with no rubber content) with increasing amounts of epoxy type B.

Moisture diffusivity is higher in the test solutions with high salt content (0.5 M and 1 M NaCl solutions) than in those with low salt content (distilled water, 100 ppm and 1000 ppm NaCl solutions) for adhesive specimens containing epoxy type A. However, no significant effect of salt concentration on diffusion rate was observed for epoxy type B.

As expected based on the above conclusions, maximum moisture absorption amount and moisture diffusivity in epoxy with 9 wt% rubber which is a mixture of epoxy type A and epoxy type B are in between those in each epoxy type.

Aluminum filler incorporation in the adhesive does not appear to have any significant effect on moisture diffusivity. However, addition of aluminum particles into the adhesive results in a decrease in the amount of moisture absorbed by decreasing the available volume for moisture diffusion (as also concluded by Al-Harthi (2003) in his thesis).

Inclusion of aluminum filler in epoxy does not affect its adhesion strength significantly in any of the environments studied (atmosphere, distilled water and sea water). Rubber modification of epoxy adhesive does not affect its adhesion strength either if not exposed to detrimental environments.

The adhesive strength does not degrade in the Gulf atmosphere for as long as 10 months (maximum exposure time applied in this study). However, degradation of the epoxy adhesive with or without rubber content is significant in distilled water or sea water. Degradation starts earlier in sea water than in distilled water. Levels of degradation in both environments are, however, similar at high exposure times (10 months).

Inclusion of rubber in the epoxy results in more significant degradation relative to that of the base epoxy in distilled water. However, rubber inclusion in the epoxy does not affect its degradation level in sea water. The epoxy adhesives degrade similarly in sea water with or without rubber content.

6. NOMENCLATURE

c: Concentration.

D: Diffusion Coefficient.

E: Potential Energy.

ΔH_v : Molar Heat of Vaporization.

j: Mass flux.

k: A constant characteristic of a pair of molecules.

l: Thickness.

M_t: Mass of diffusant intake at time t

M_∞: Mass of diffusant intake at saturation.

r: Distance of separation of two molecules.

R: Gas Constant.

T: Temperature.

t: Time.

V: Molar Volume.

δ: Solubility Parameter.

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APPENDICES

APPENDIX A

Preparation of Adhesive Specimens for the Moisture Diffusion Tests

Preparation of Adhesive Specimens for the Moisture Diffusion Tests

1. Prepare 30×80 mm^2 metal sheets of any thickness and 40×7×1.0 mm^3 metal strips.
2. Wrap the metal sheets with wax paper.
3. Prepare epoxy adhesive first as base free from fillers and then after addition of rubber and aluminum filler at several fractions.
4. Place two metal strips at the edges of a wax paper wrapped metal sheet and spread the adhesive on the surface between the metal strips with a thickness little over 1.0 mm.
5. Place another wax paper wrapped metal sheet on the top and clamp the two sheets together.
6. Remove the excess adhesive at the sides.
7. Release the clamp after about 24 hours and cut the molded adhesive sheet into three 30×30×1.0 mm^3 square sheets.

APPENDIX B

Adhesive Joint Surface Preparation

Adhesive Joint Surface Preparation

1. Degrease by dipping in trichloroethylene and isopropyl alcohol, separately.
2. Wash with water.
3. Roughen their surfaces by abrader cleaning (mechanical cleaning) by 400 Grit Silicon Carbide Grinding paper.
4. Degrease by dipping in trichloroethylene and isopropyl alcohol (30 min each).
5. Immerse for 2-4 hr in a solution of H_2SO_4, sodium dichromate and distilled water in proportion: 22.5, 7.5, and 70 by weight, respectively. (Chromic-sulphuric etching process).
6. Wash with distilled water.
7. Dry them with clean tissue and keep in desiccators (making sure they are dry).

References: [Semerdjiev, 1970; Kozma and Olefjord, 1987; Prakash, et al., 1987]

APPENDIX C

Diffusivity Determination by Use of Equation 22

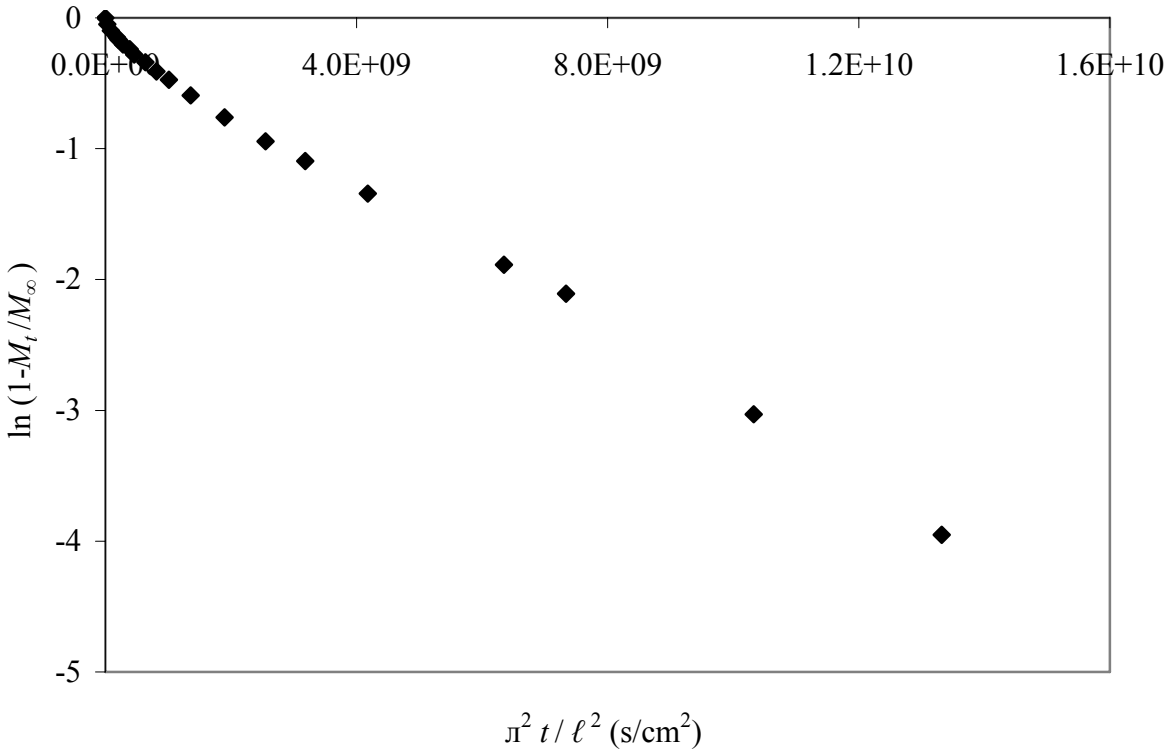

Figure C1. Representative plot of ln(1-M_t/M_∞) vs. (л^2 t/ ℓ^2) for epoxy adhesive with no filler in distilled water.

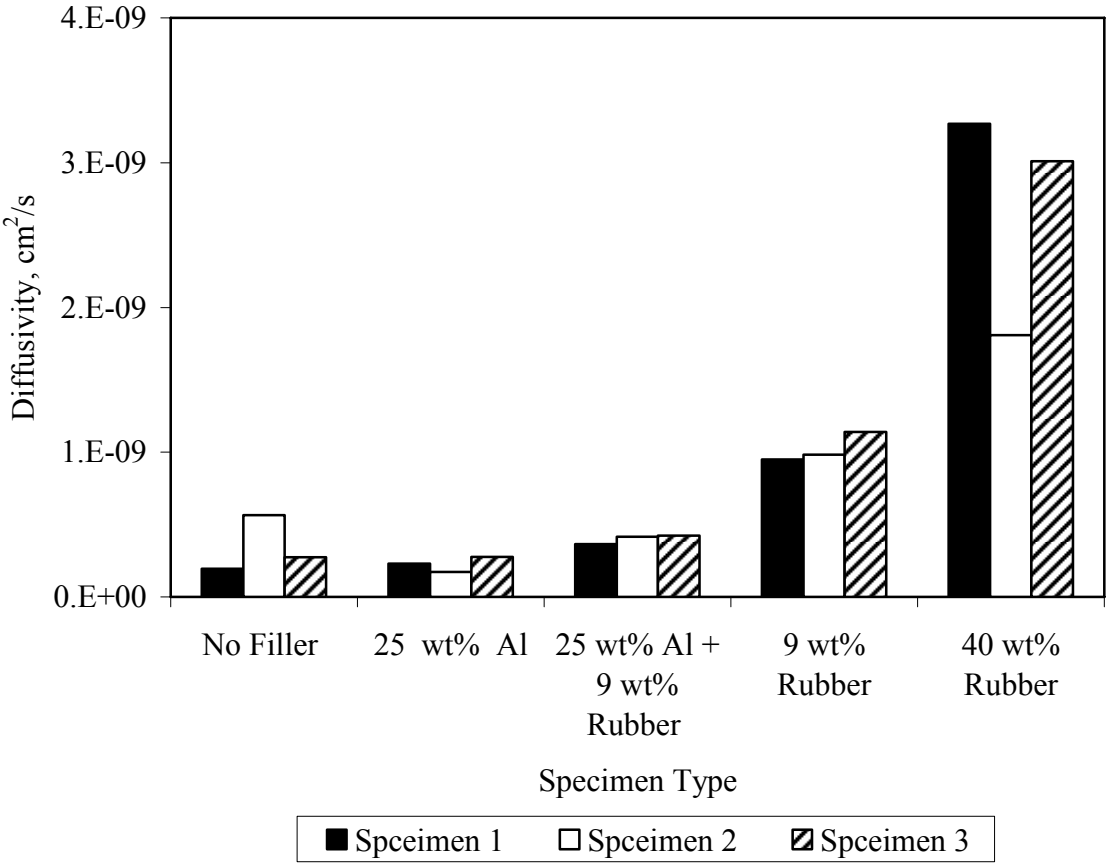

Figure C2. Diffusivity in distilled water (determined by use of Equation 22) vs. specimen type.

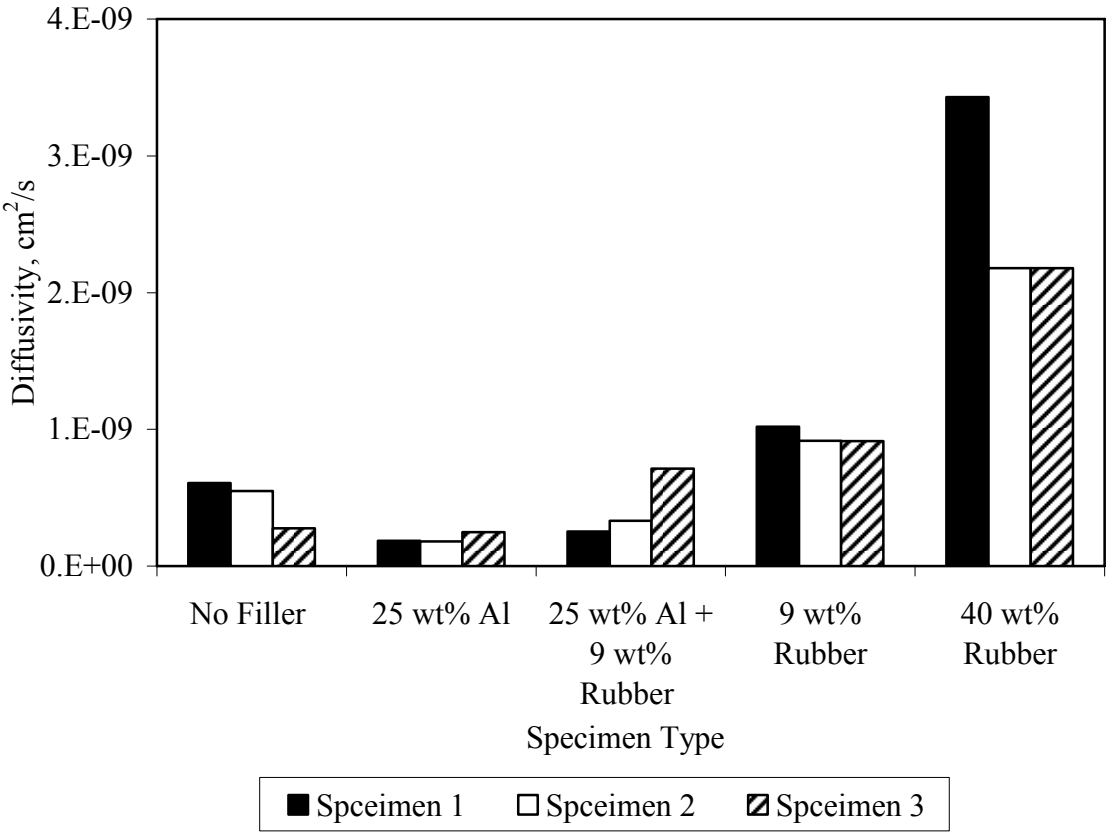

Figure C3. Diffusivity in 100 ppm NaCl solution (determined by use of Equation 22) vs. specimen type.

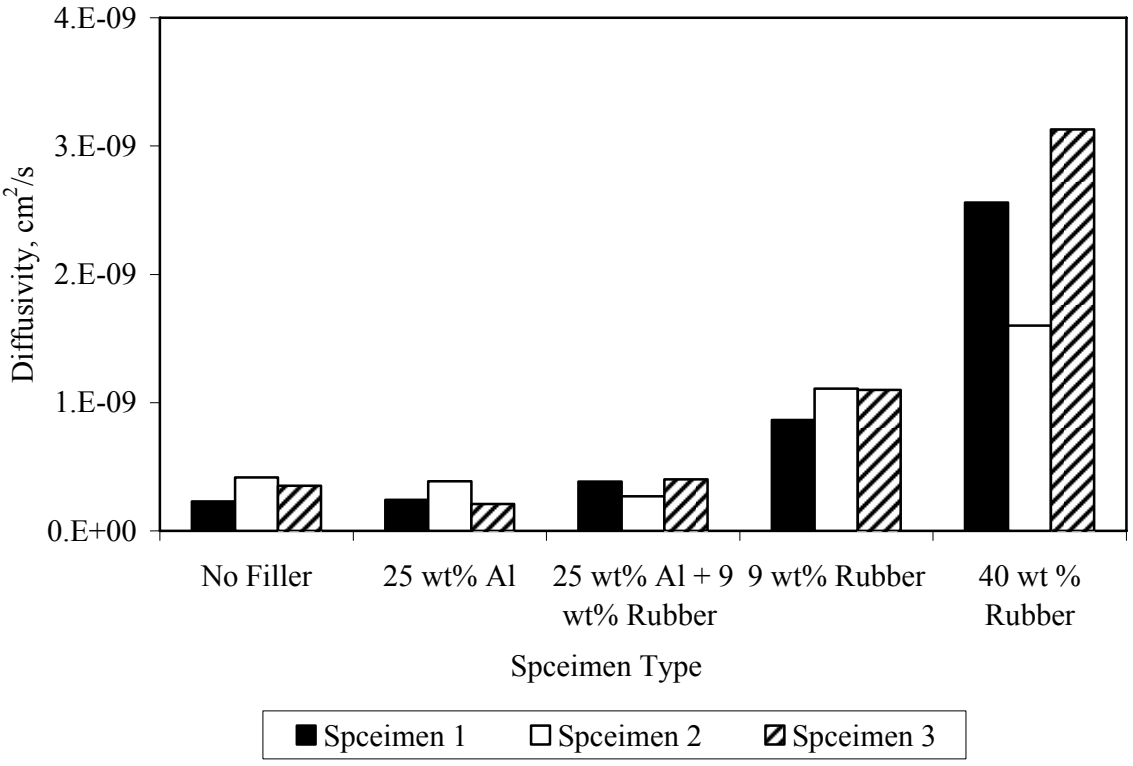

Figure C4. Diffusivity in 1000 ppm NaCl solution (determined by use of Equation 22) vs. specimen type.

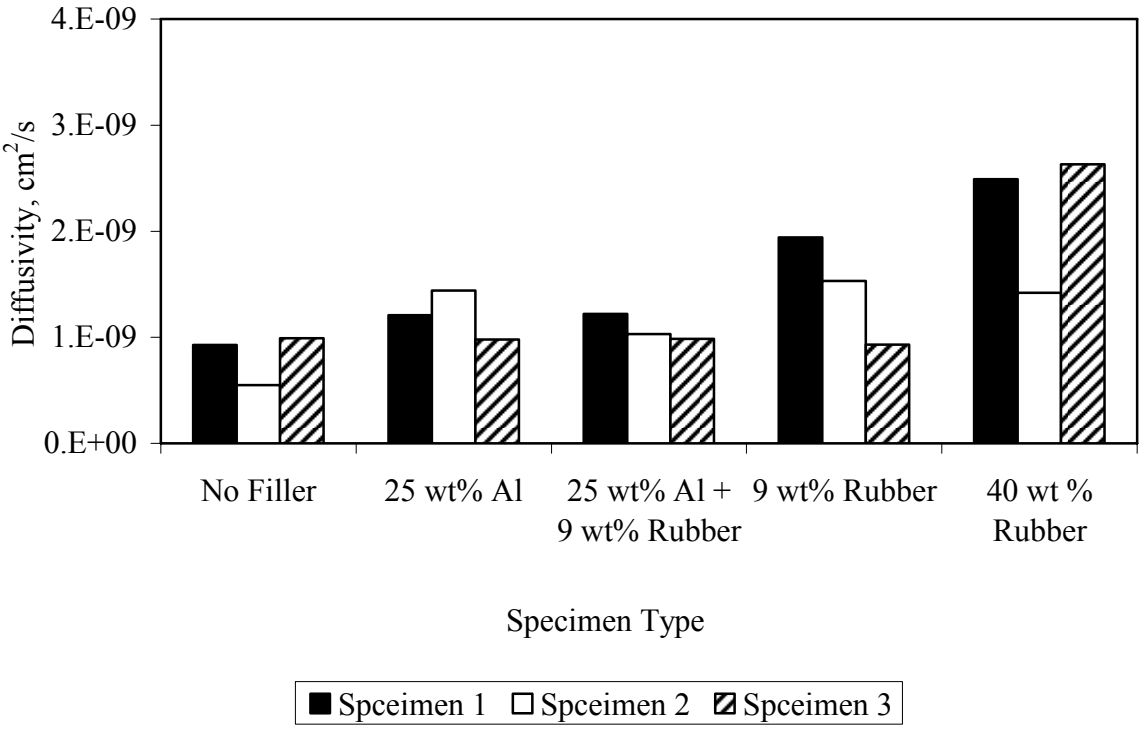

Figure C5. Diffusivity in 0.5 M NaCl solution (determined by use of Equation 22) vs. specimen type.

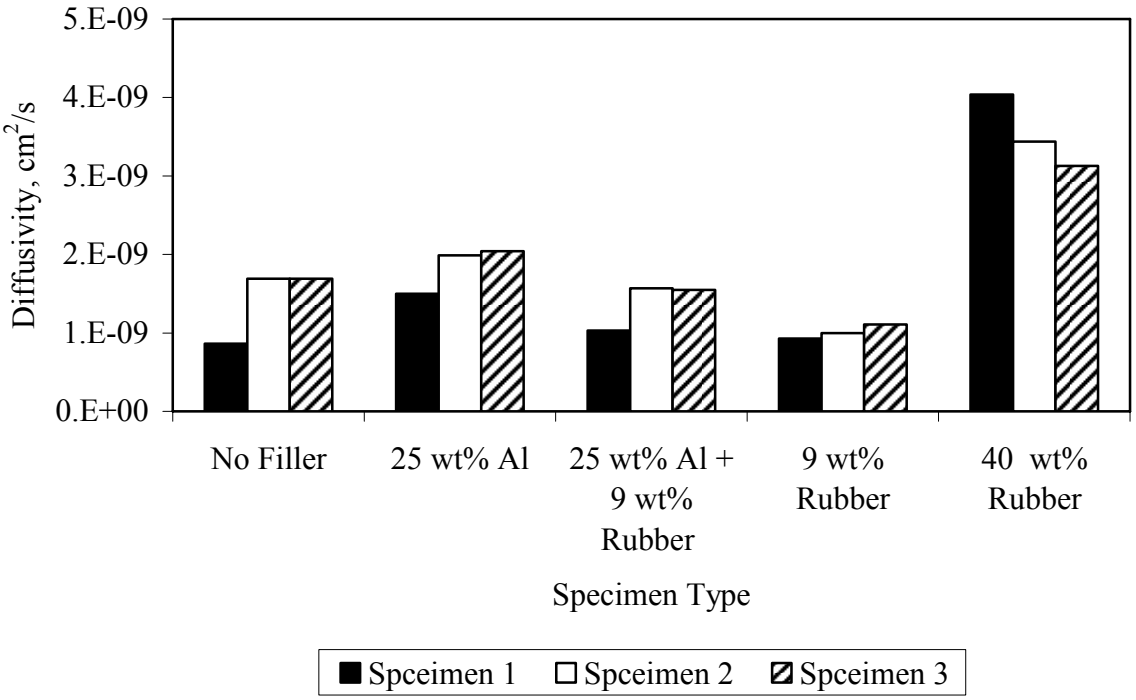

Figure C6. Diffusivity in 1 M NaCl solution (determined by use of Equation 22) vs. specimen type.

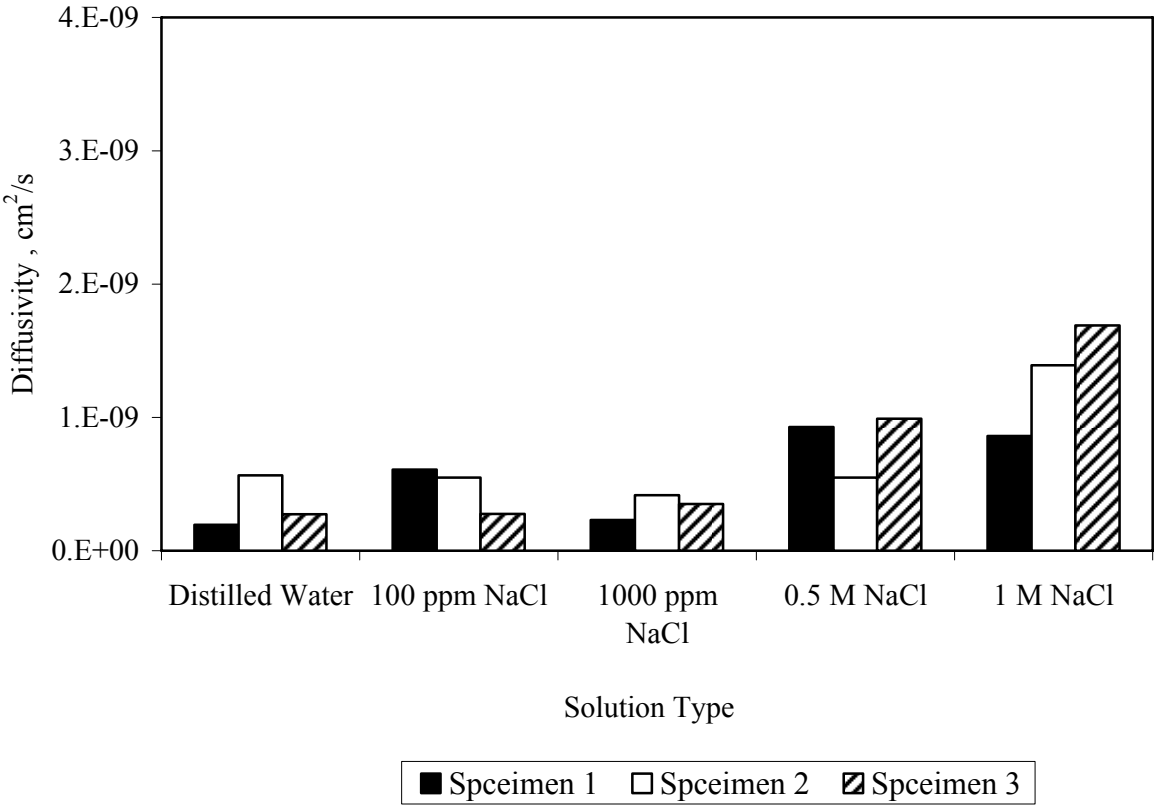

Figure C7. Diffusivity in epoxy adhesive with no filler (determined by use of Equation 22) vs. solution type.

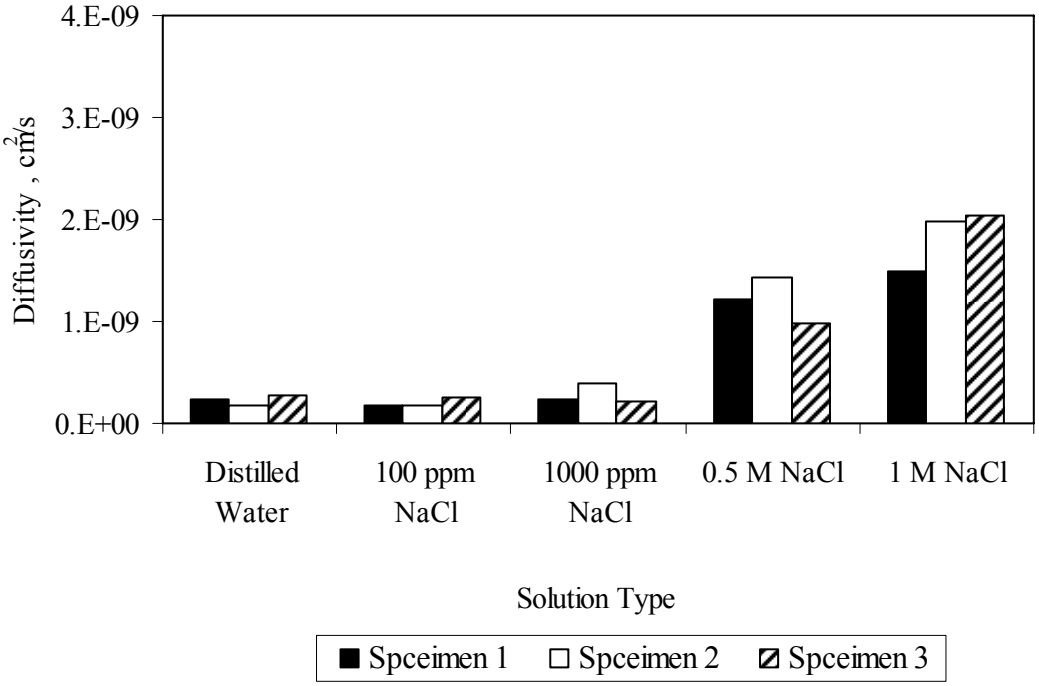

Figure C8. Diffusivity in epoxy adhesive with 25 wt% aluminum filler (determined by use of Equation 22) vs. solution type.

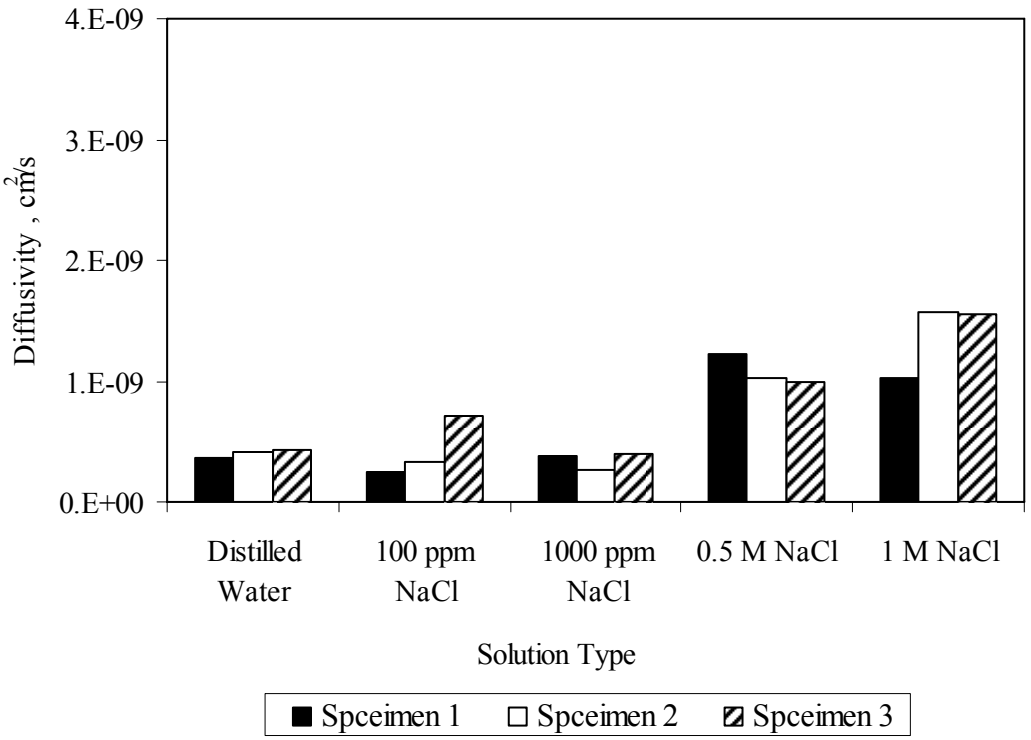

Figure C9. Diffusivity in epoxy adhesive with 9 wt% rubber and 25 wt% aluminum filler (determined by use of Equation 22) vs. solution type.

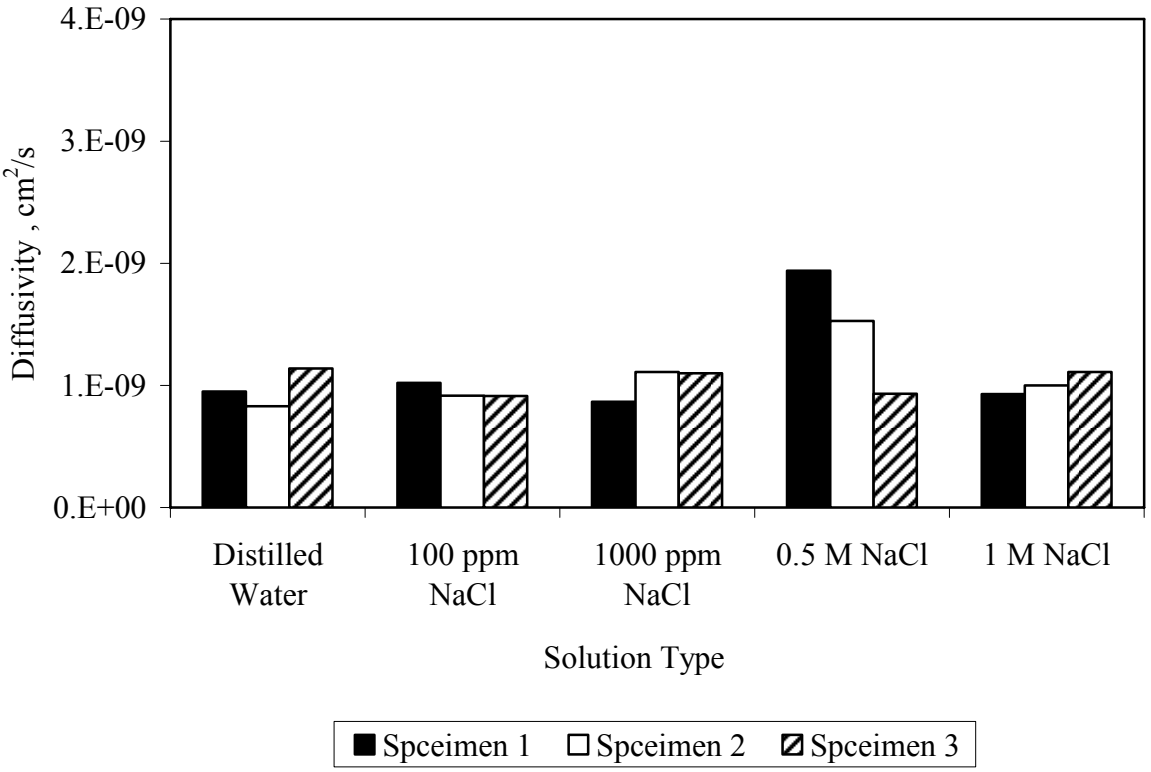

Figure C10. Diffusivity in epoxy adhesive with 9 wt% rubber (determined by use of Equation 22) vs. solution type.

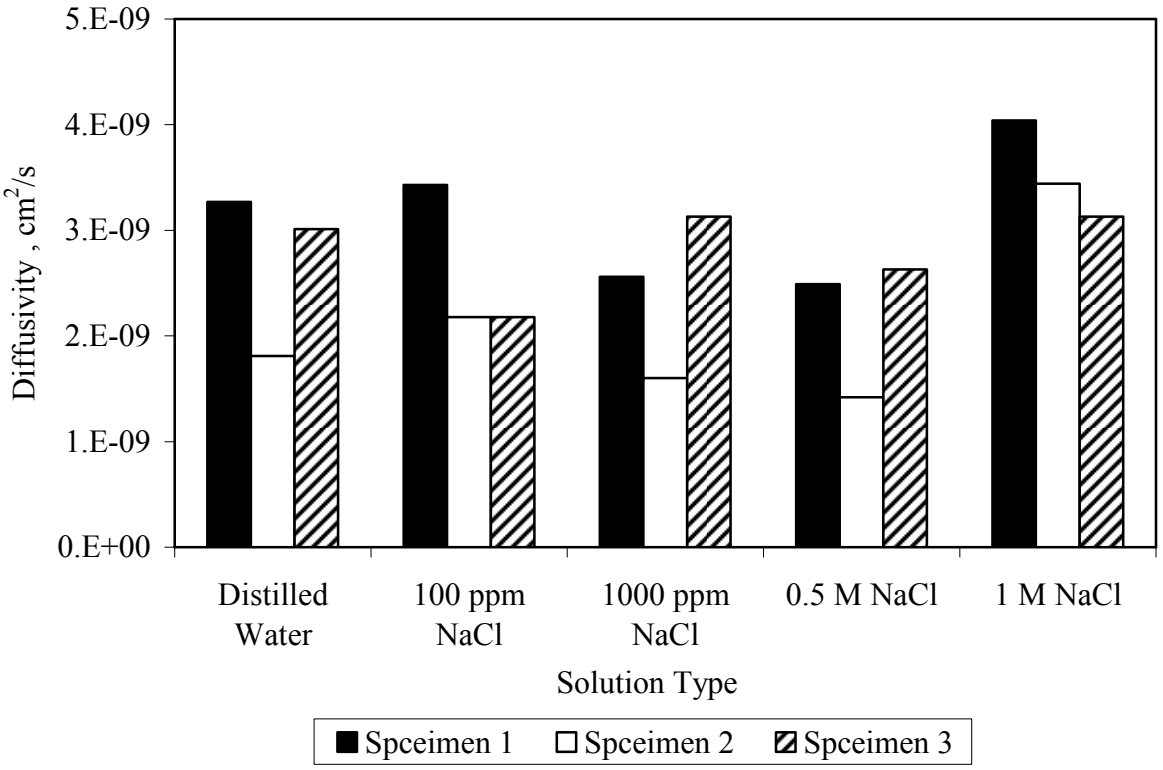

Figure C11. Diffusivity in epoxy adhesive with 40 wt% rubber (determined by use of Equation 22) vs. solution type.

Appendix D

Tables of Diffusivity Data

Table D1. Moisture diffusivity data for epoxy adhesive with no filler.

Solution	Run #	Diffusivity by Equation 20 (cm^2/s)	Diffusivity by Equation 22 (cm^2/s)
Distilled Water	1	1.80E-10	1.95E-10
	2	1.93E-10	5.65E-10
	3	2.16E-10	2.74E-10
	Average	1.96E-10	3.45E-10
100 ppm NaCl Solution	1	4.88E-10	6.09E-10
	2	4.37E-10	5.50E-10
	3	3.46E-10	2.76E-10
	Average	4.24E-10	4.78E-10
1000 ppm NaCl Solution	1	2.37E-10	2.30E-10
	2	3.03E-10	4.17E-10
	3	3.24E-10	3.51E-10
	Average	2.88E-10	3.33E-10
0.5 M NaCl Solution	1	8.12E-10	9.28E-10
	2	6.35E-10	5.49E-10
	3	7.56E-10	9.91E-10
	Average	7.35E-10	8.23E-10
1 M NaCl Solution	1	5.76E-10	8.62E-10
	2	6.10E-10	1.39E-09
	3	3.73E-09	1.69E-09
	Average	1.64E-09	1.31E-09

Table D2. Moisture diffusivity data for epoxy adhesive with 25 wt% aluminum filler content.

Solution	Run #	Diffusivity by Equation 20 (cm^2/s)	Diffusivity by Equation 22 (cm^2/s)
Distilled Water	1	2.34E-10	2.29E-10
	2	1.93E-10	1.72E-10
	3	2.22E-10	2.75E-10
	Average	2.16E-10	2.25E-10
100 ppm NaCl Solution	1	1.77E-10	1.84E-10
	2	6.89E-11	1.81E-10
	3	1.69E-10	2.47E-10
	Average	1.38E-10	2.04E-10
1000 ppm NaCl Solution	1	1.32E-10	2.42E-10
	2	2.59E-10	3.87E-10
	3	1.80E-10	2.09E-10
	Average	1.90E-10	2.79E-10
0.5 M NaCl Solution	1	6.71E-10	1.21E-09
	2	9.73E-10	1.44E-09
	3	6.92E-10	9.80E-10
	Average	7.79E-10	1.21E-09
1 M NaCl Solution	1	9.73E-10	1.50E-09
	2	1.19E-09	1.99E-09
	3	1.51E-09	2.04E-09
	Average	1.22E-09	1.84E-09

Table D3. Moisture diffusivity data for epoxy adhesive with 9 wt% rubber and 25 wt% aluminum filler content.

Solution	Run #	Diffusivity by Equation 20 (cm^2/s)	Diffusivity by Equation 22 (cm^2/s)
Distilled Water	1	2.82E-10	3.64E-10
	2	4.24E-10	4.16E-10
	3	4.28E-10	4.25E-10
	Average	3.78E-10	4.02E-10
100 ppm NaCl Solution	1	3.84E-10	2.53E-10
	2	5.81E-10	3.32E-10
	3	5.81E-10	7.14E-10
	Average	5.15E-10	4.33E-10
1000 ppm NaCl Solution	1	4.88E-10	3.83E-10
	2	2.62E-10	2.69E-10
	3	2.50E-10	4.02E-10
	Average	3.33E-10	3.51E-10
0.5 M NaCl Solution	1	1.06E-09	1.22E-09
	2	8.82E-10	1.03E-09
	3	9.00E-10	9.86E-10
	Average	9.46E-10	1.08E-09
1 M NaCl Solution	1	9.12E-10	1.03E-09
	2	1.23E-09	1.57E-09
	3	1.35E-09	1.55E-09
	Average	1.16E-09	1.38E-09

Table D4. Moisture diffusivity data for epoxy adhesive with 9 wt% rubber.

Solution	Run #	Diffusivity by Equation 20 (cm^2/s)	Diffusivity by Equation 22 (cm^2/s)
Distilled Water	1	7.62E-10	9.49E-10
	2	6.60E-10	9.83E-10
	3	7.84E-10	1.14E-09
	Average	7.35E-10	1.02E-09
100 ppm NaCl Solution	1	5.62E-10	1.02E-09
	2	6.55E-10	9.17E-10
	3	6.35E-10	9.14E-10
	Average	6.17E-10	9.16E-10
1000 ppm NaCl Solution	1	7.18E-10	8.66E-10
	2	9.24E-10	1.11E-09
	3	9.06E-10	1.10E-09
	Average	8.49E-10	1.03E-09
0.5 M NaCl Solution	1	9.00E-10	1.94E-09
	2	1.17E-09	1.53E-09
	3	7.45E-10	9.31E-10
	Average	9.38E-10	1.47E-09
1 M NaCl Solution	1	8.24E-10	9.30E-10
	2	8.94E-10	1.00E-09
	3	9.42E-10	1.11E-09
	Average	8.87E-10	1.01E-09

Table D5. Moisture diffusivity data for epoxy adhesive with 40 wt% rubber.

Solution	Run #	Diffusivity by Equation 20 (cm^2/s)	Diffusivity by Equation 22 (cm^2/s)
Distilled Water	1	3.42E-09	3.27E-09
	2	1.89E-09	1.81E-09
	3	3.09E-09	3.01E-09
	Average	2.80E-09	2.70E-09
100 ppm NaCl Solution	1	3.78E-09	3.43E-09
	2	2.29E-09	2.18E-09
	3	2.16E-09	2.18E-09
	Average	2.75E-09	2.60E-09
1000 ppm NaCl Solution	1	3.29E-09	2.56E-09
	2	1.00E-09	1.60E-09
	3	7.41E-09	3.13E-09
	Average	3.90E-09	2.43E-09
0.5 M NaCl Solution	1	2.83E-09	2.49E-09
	2	1.54E-09	1.42E-09
	3	2.40E-09	2.63E-09
	Average	2.26E-09	2.18E-09
1 M NaCl Solution	1	4.07E-09	4.04E-09
	2	4.29E-09	3.44E-09
	3	3.58E-09	3.13E-09
	Average	3.98E-09	3.54E-09

Appendix E

Theoretical and Experimental Fractional Uptake vs. Time Plots

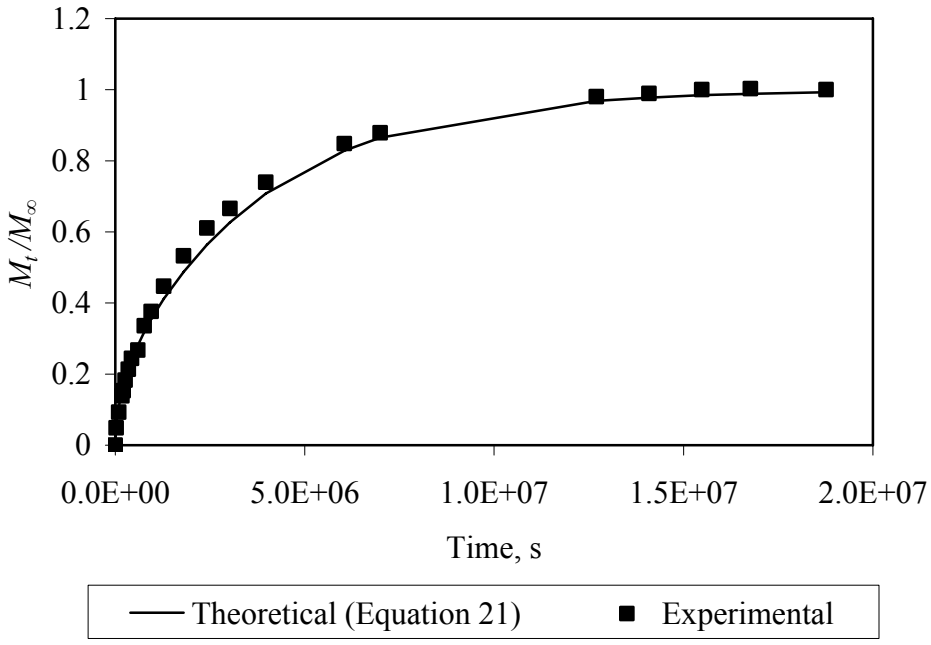

Figure E1. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with no filler in distilled water.

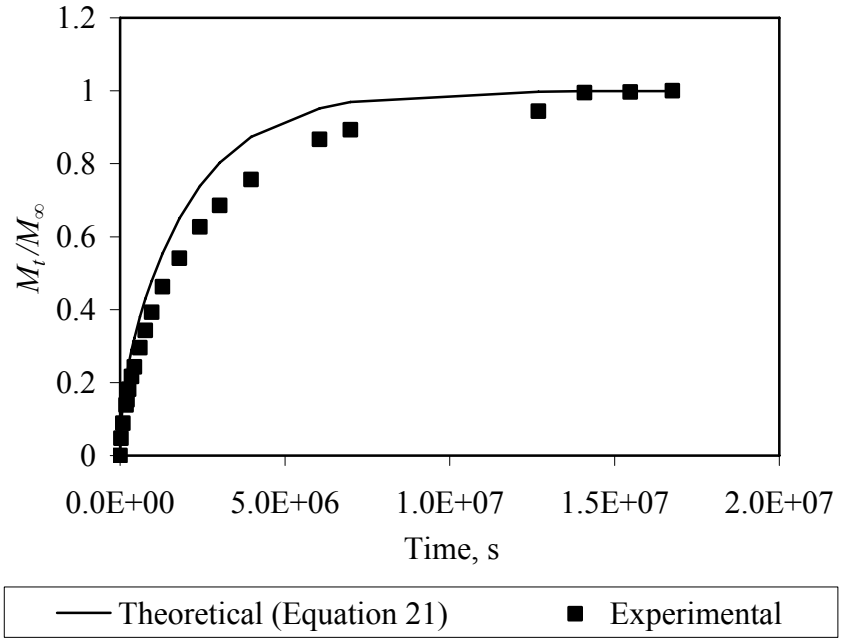

Figure E2. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with no filler in 100 ppm NaCl solution.

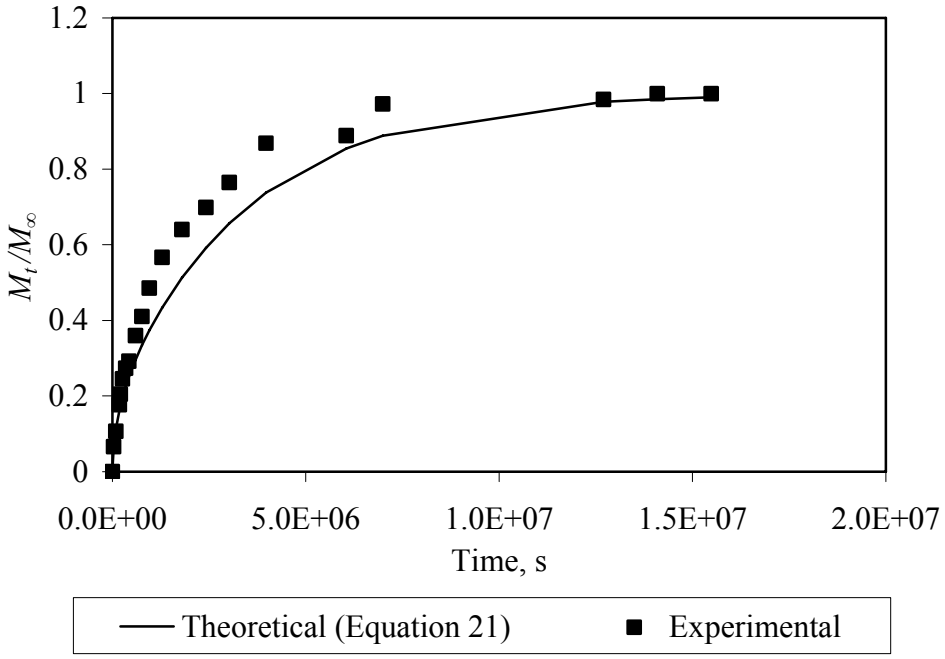

Figure E3. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with no filler in 1000 ppm NaCl solution.

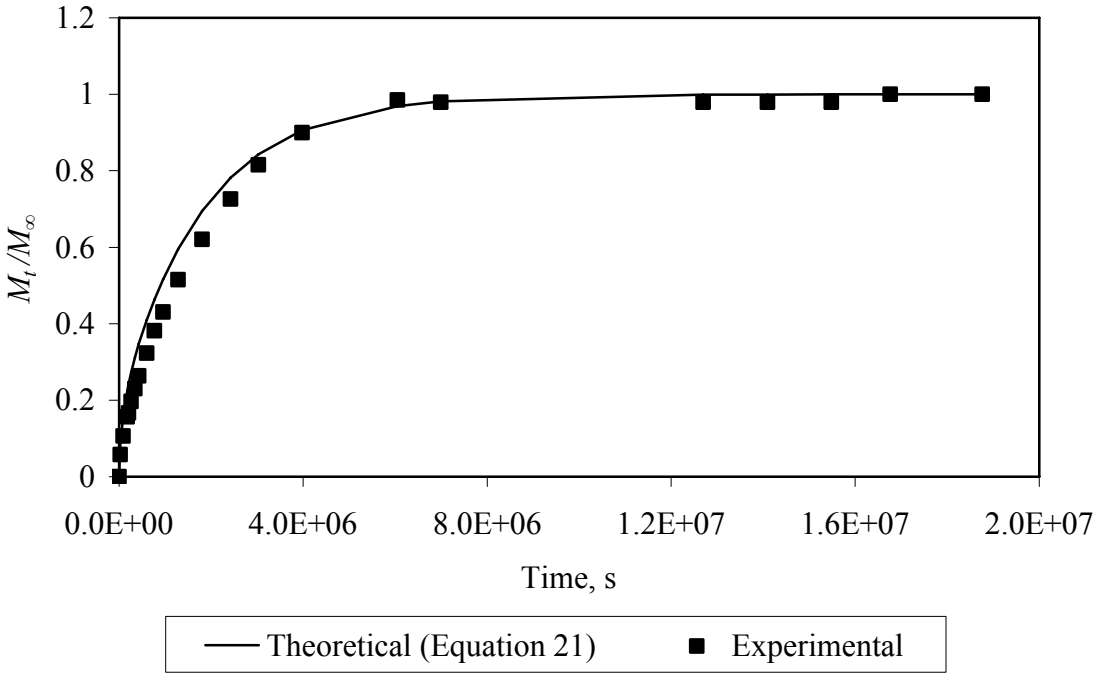

Figure E4. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with no filler in 1 M NaCl solution.

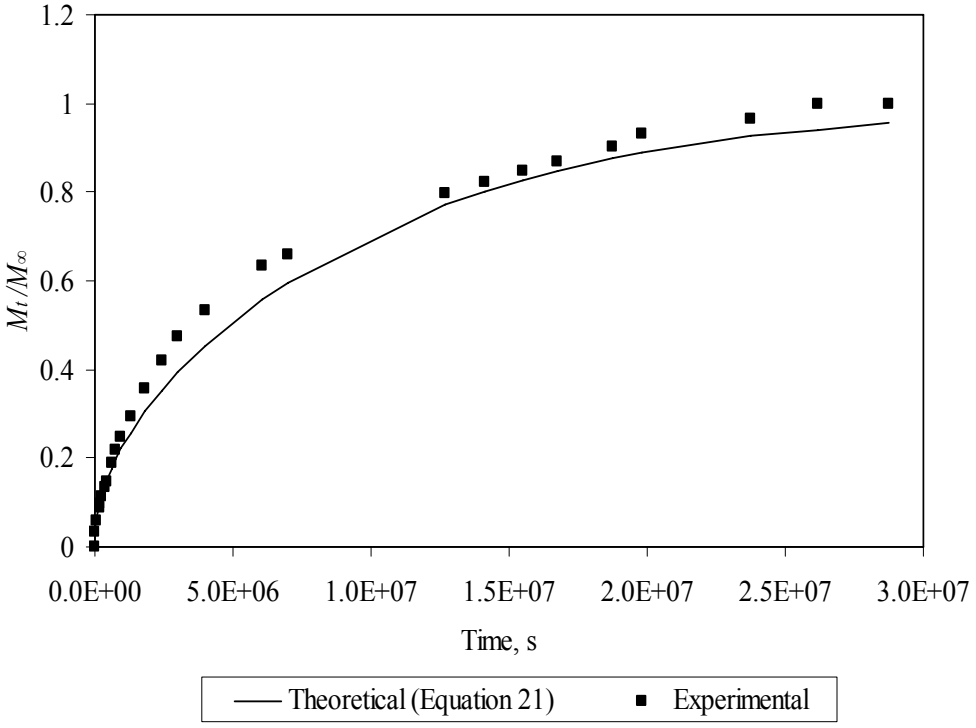

Figure E5. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 25 wt% aluminum filler in distilled water.

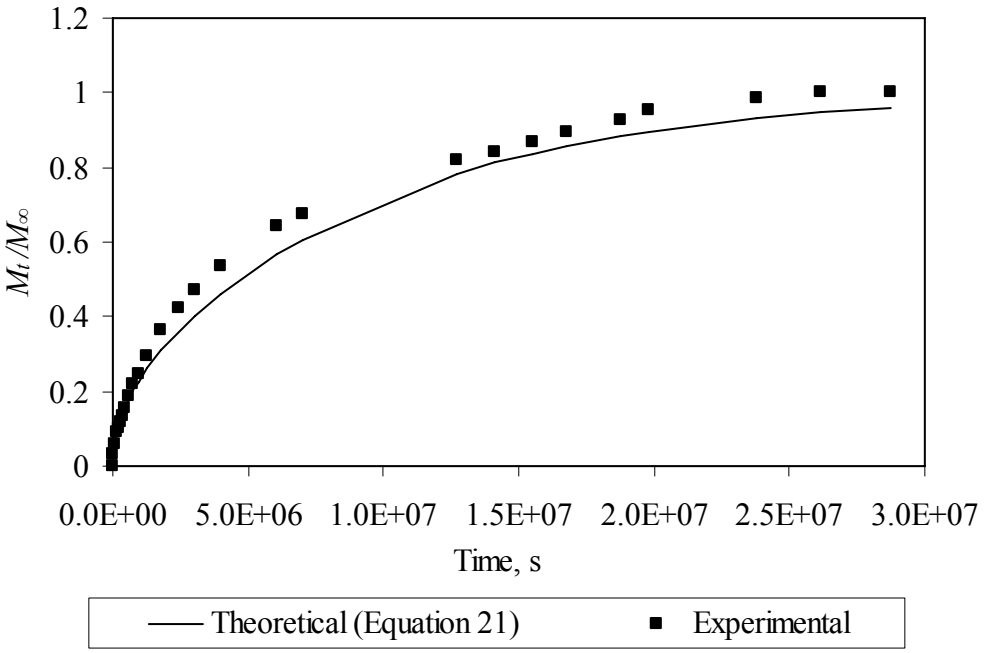

Figure E6. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 25 wt% aluminum filler in 100 ppm NaCl solution.

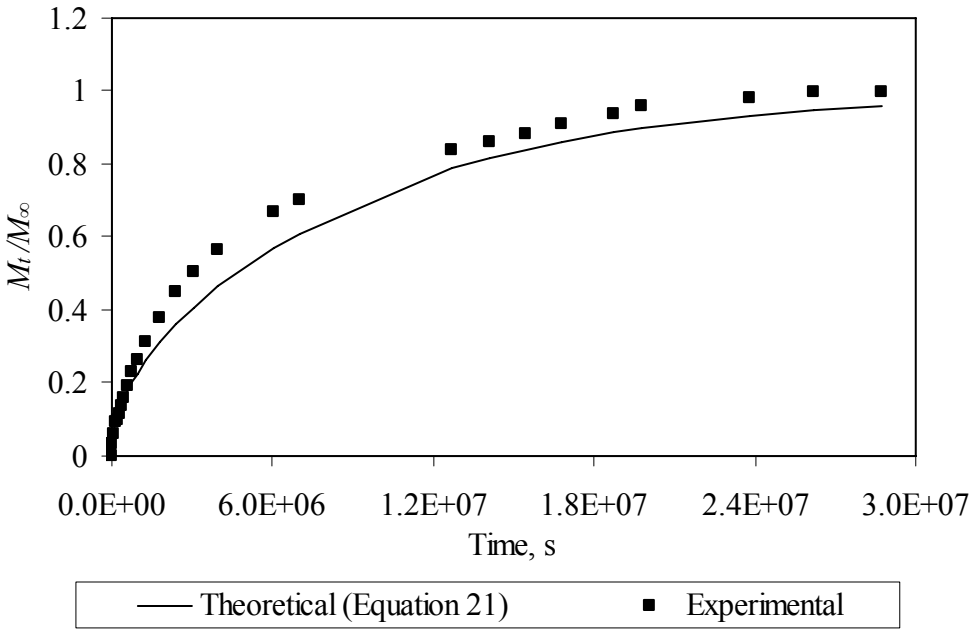

Figure E7. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 25 wt% aluminum filler in 1000 ppm NaCl solution.

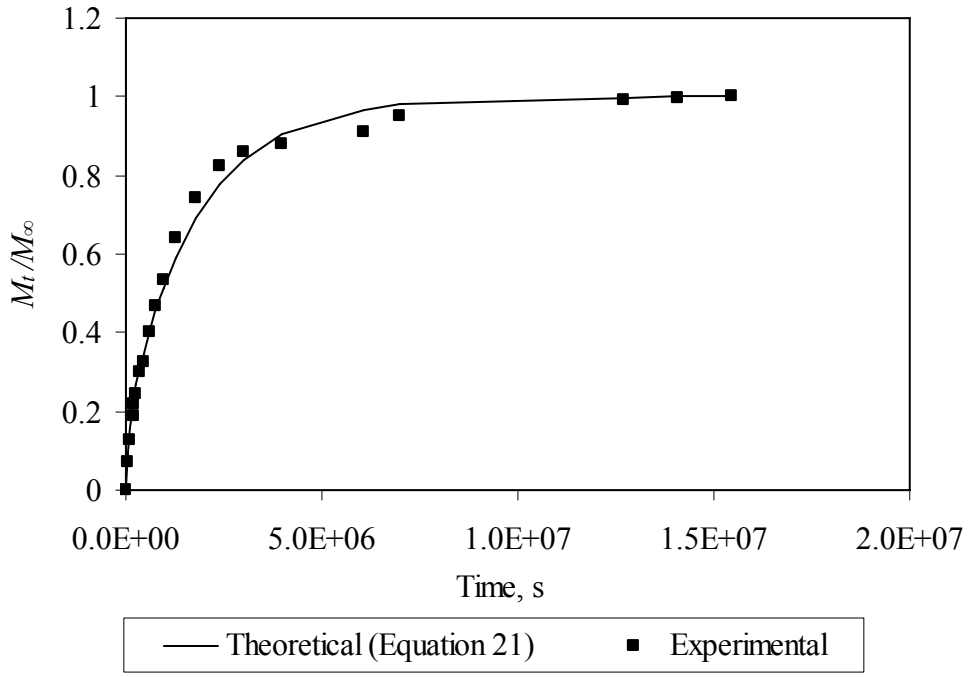

Figure E8. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 25 wt% aluminum filler in 0.5 M NaCl solution.

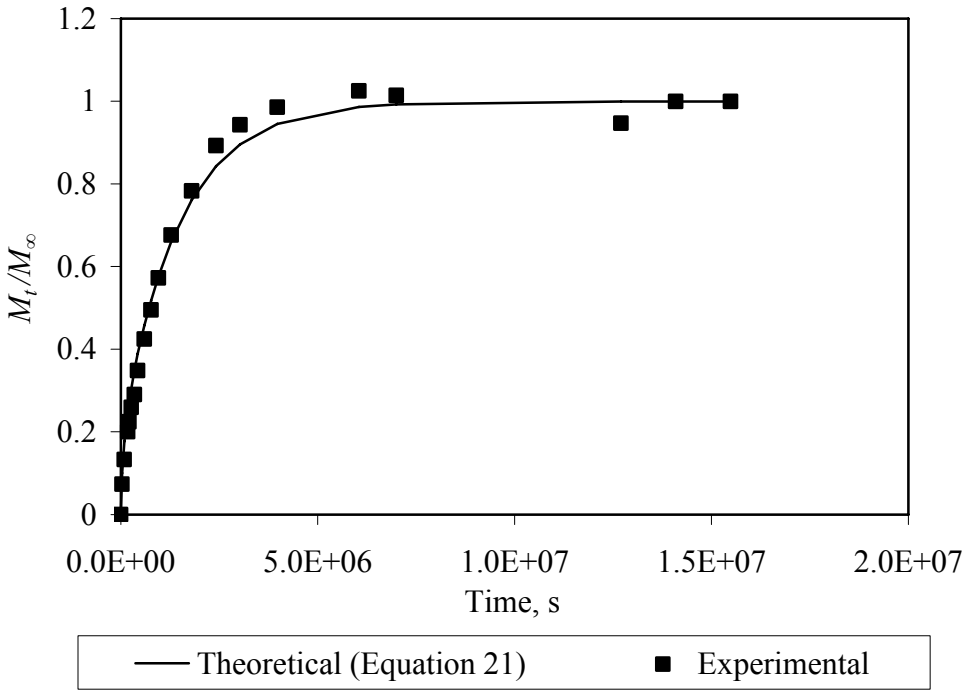

Figure E9. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 25 wt% aluminum filler in 1 M NaCl solution.

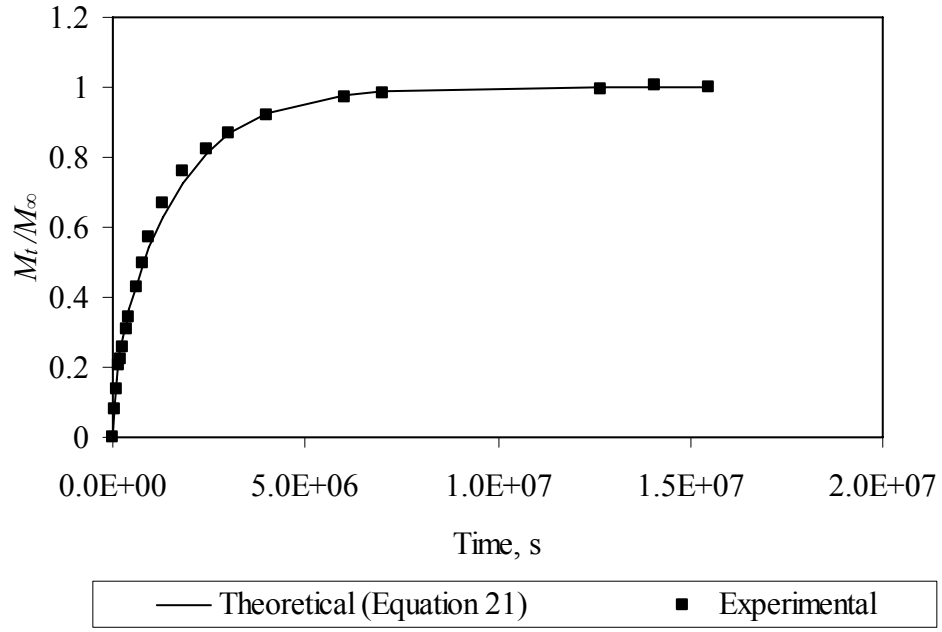

Figure E10. Theoretical and experimental fractional uptake for epoxy adhesive with 9 wt% rubber in distilled water.

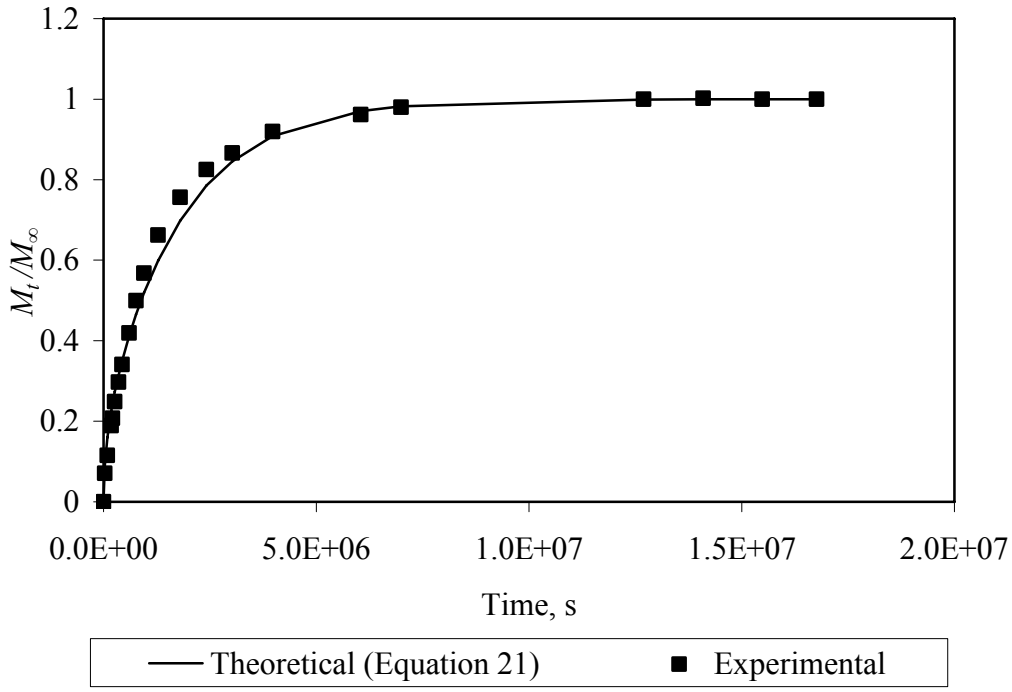

Figure E11. Theoretical and experimental fractional uptake for epoxy adhesive with 9 wt% rubber in 100 ppm NaCl solution.

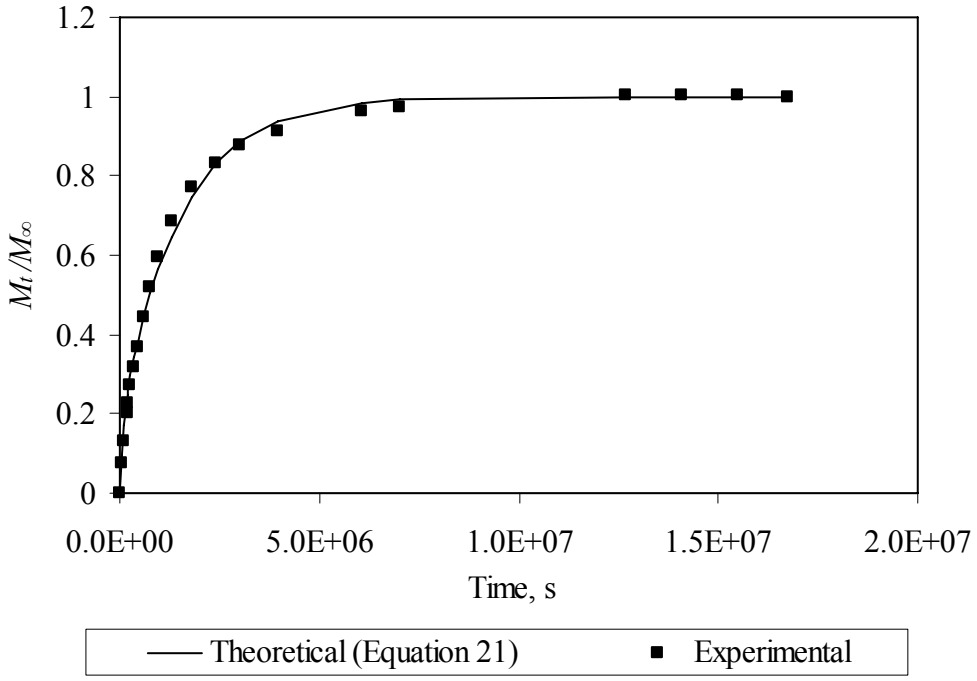

Figure E12. Theoretical and experimental fractional uptake for epoxy adhesive with 9 wt% rubber in 1000 ppm NaCl solution.

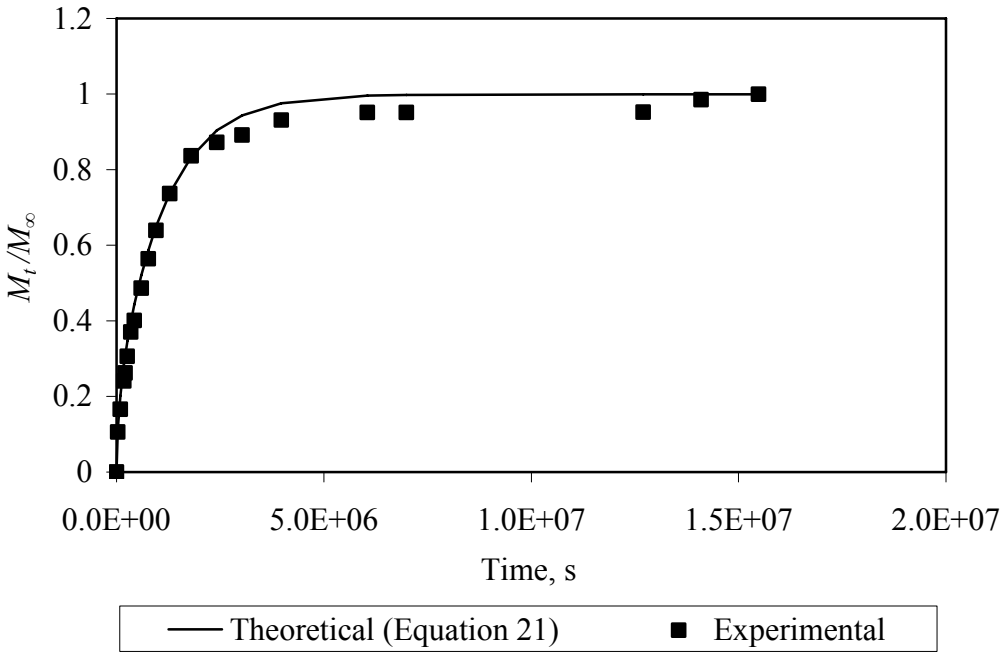

Figure E13. Theoretical and experimental fractional uptake for epoxy adhesive with 9 wt% rubber in 0.5 M NaCl solution.

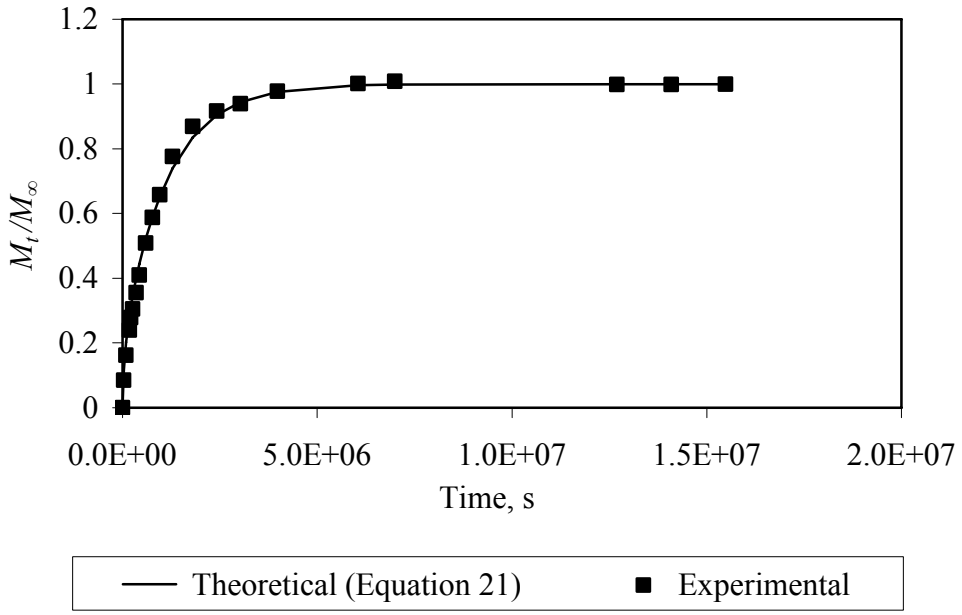

Figure E14. Theoretical and experimental fractional uptake for epoxy adhesive with 9 wt% rubber in 1 M NaCl solution.

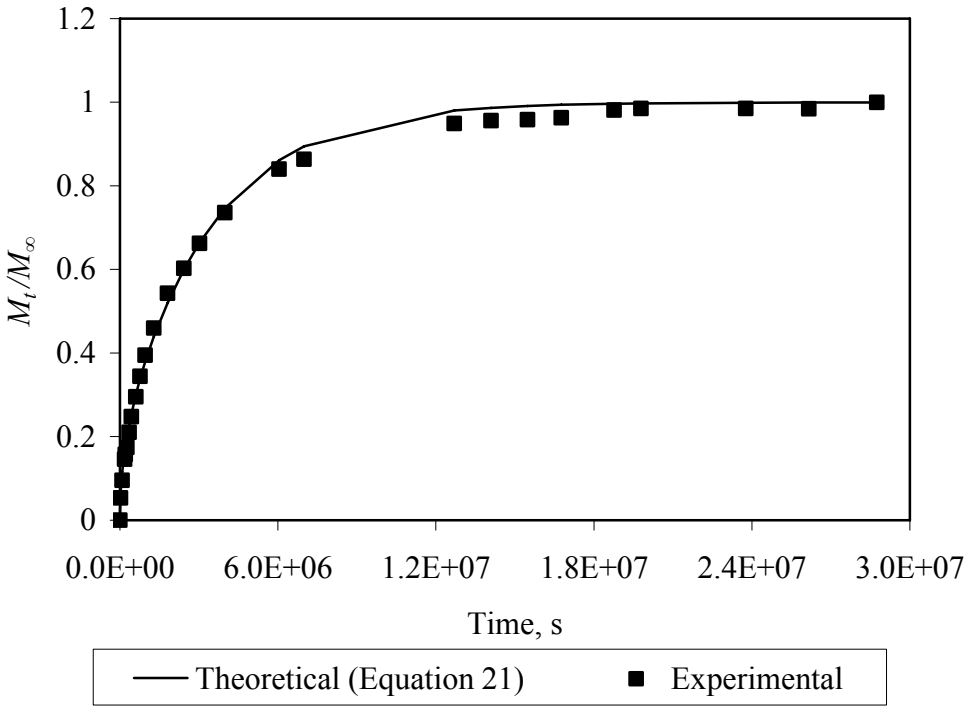

Figure E15. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 25 wt% aluminum and 9 wt% rubber in distilled water.

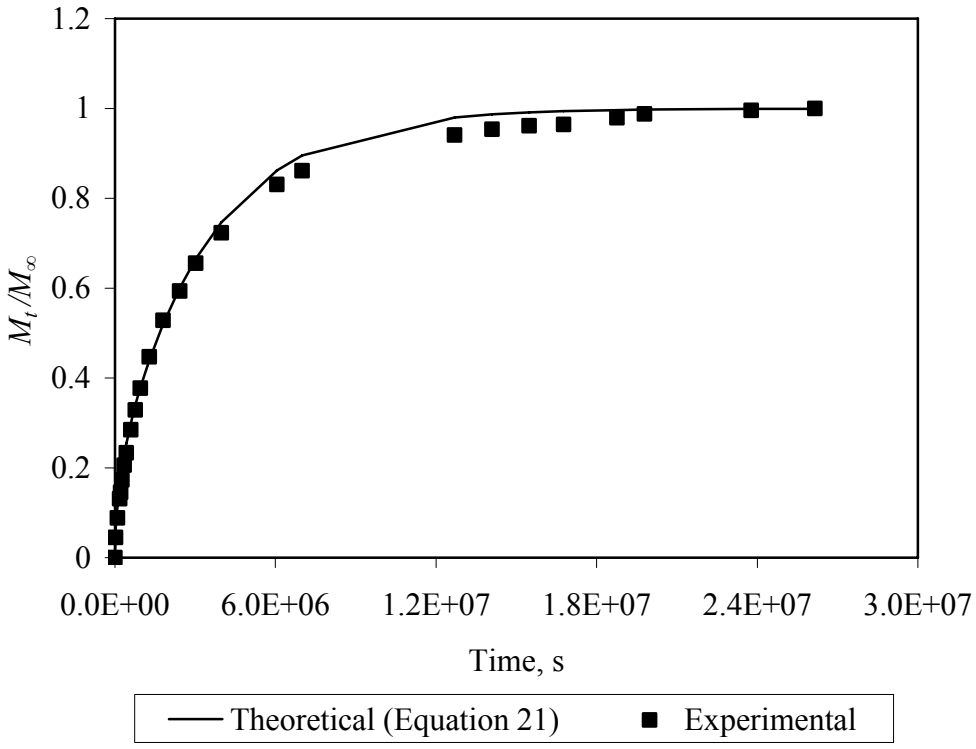

Figure E16. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 25 wt% aluminum and 9 wt% rubber in 100 ppm NaCl solution.

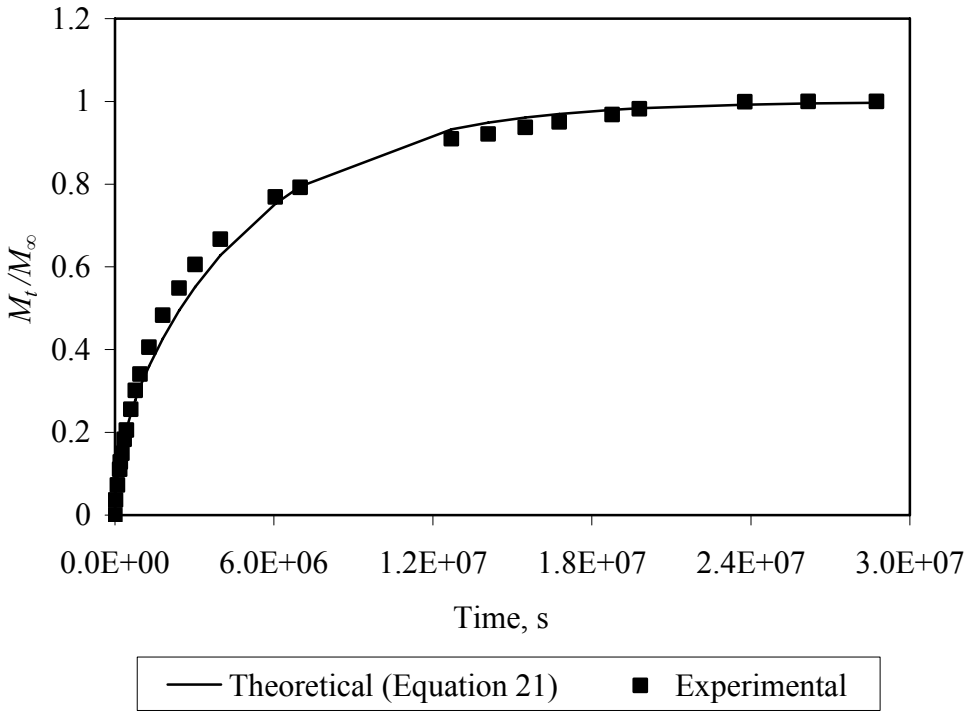

Figure E17. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 25 wt% aluminum and 9 wt% rubber in 1000 ppm NaCl solution.

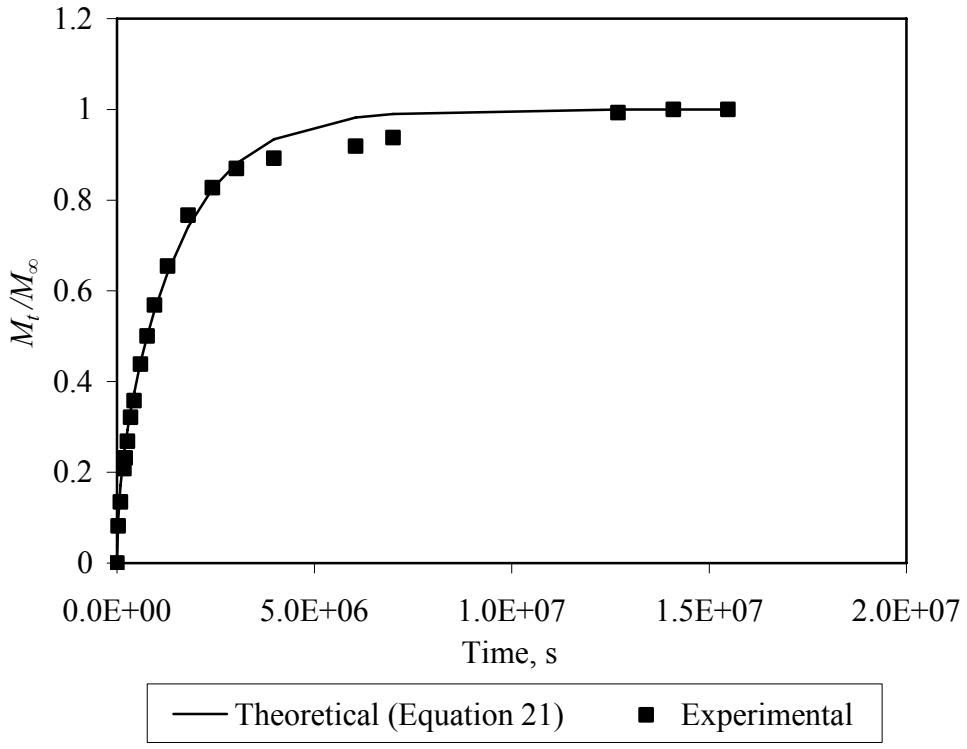

Figure E18. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 25 wt% aluminum and 9 wt% rubber in 0.5 M NaCl solution.

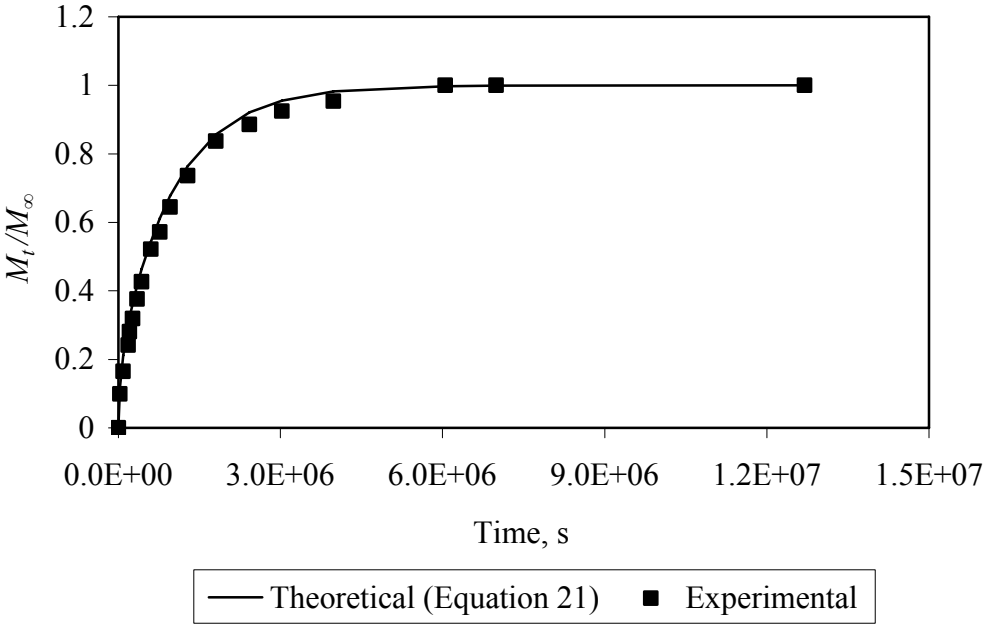

Figure E19. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 25 wt% aluminum and 9 wt% rubber in 1 M NaCl solution.

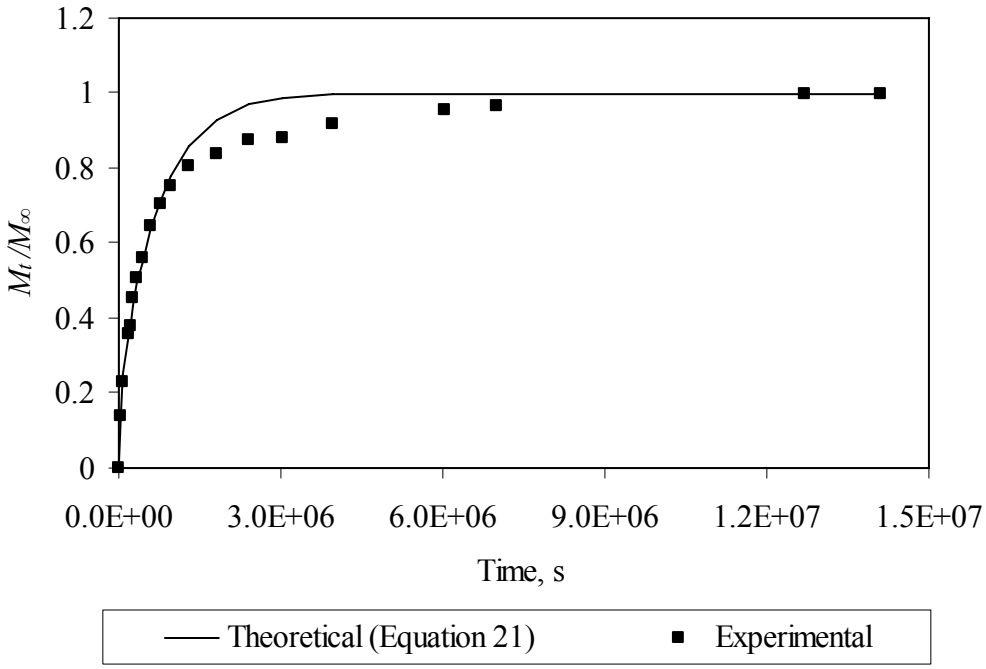

Figure E20. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 40 wt% rubber in distilled water.

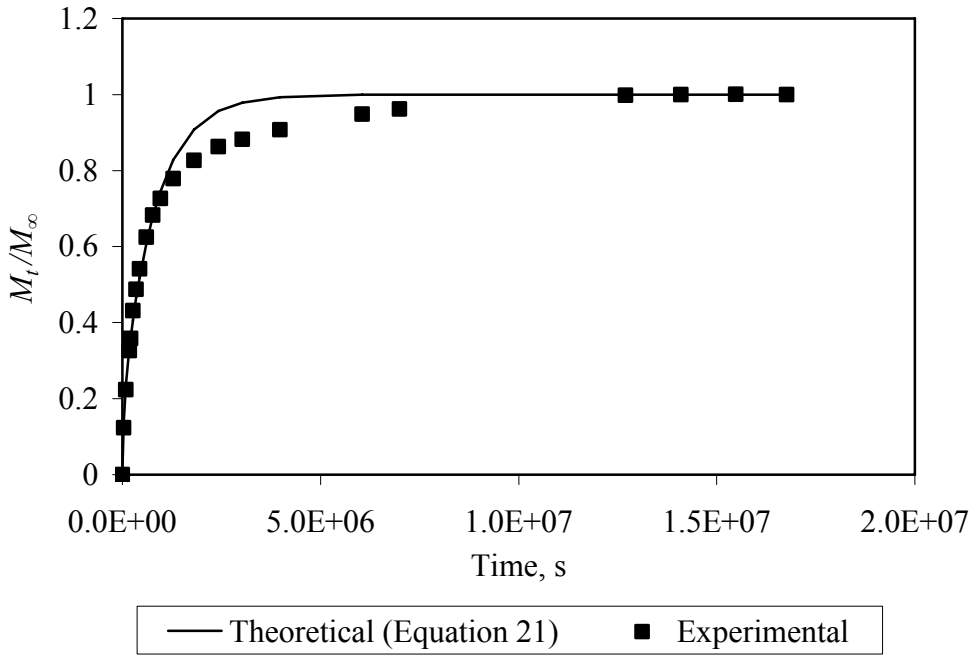

Figure E21. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 40 wt% rubber in 100 ppm NaCl solution.

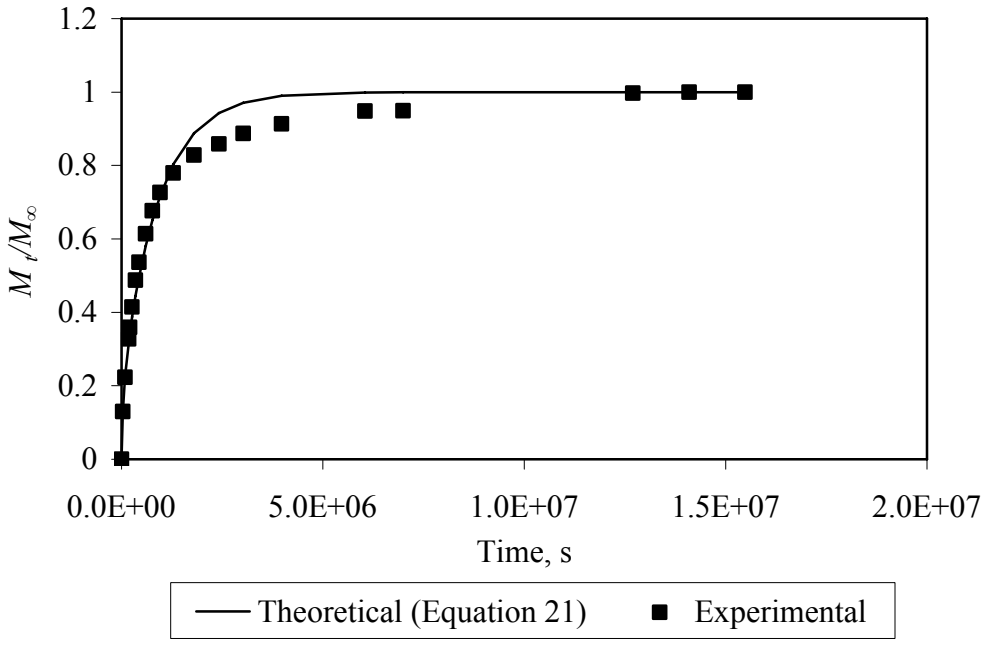

Figure E22. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 40 wt% rubber in 1000 ppm NaCl solution.

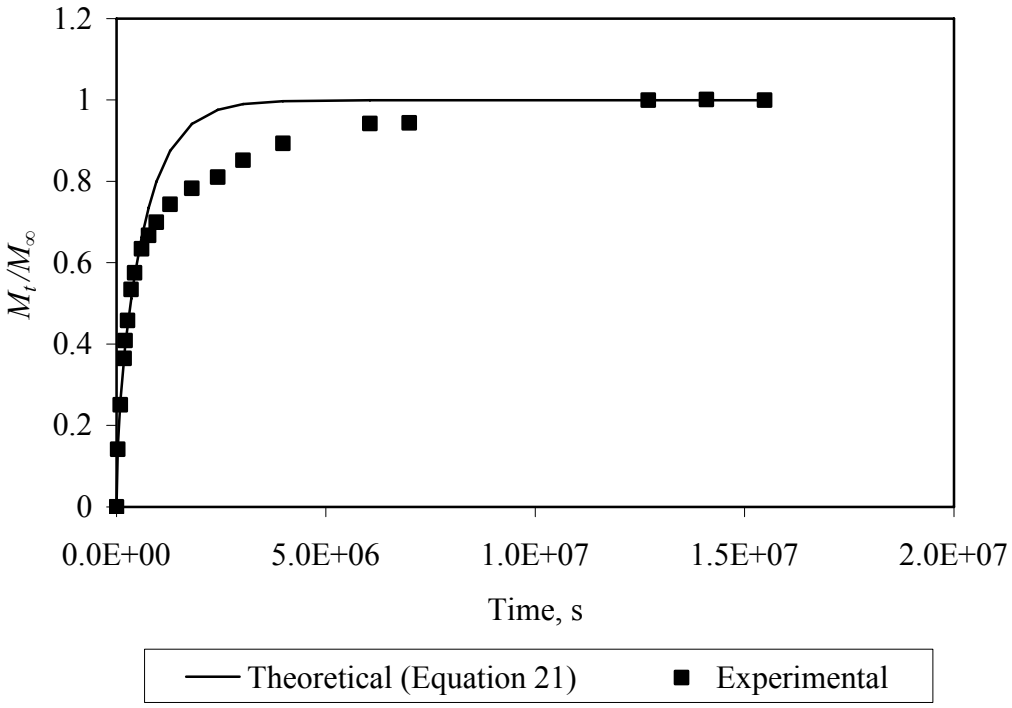

Figure E23. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 40 wt% rubber in 0.5 M NaCl solution.

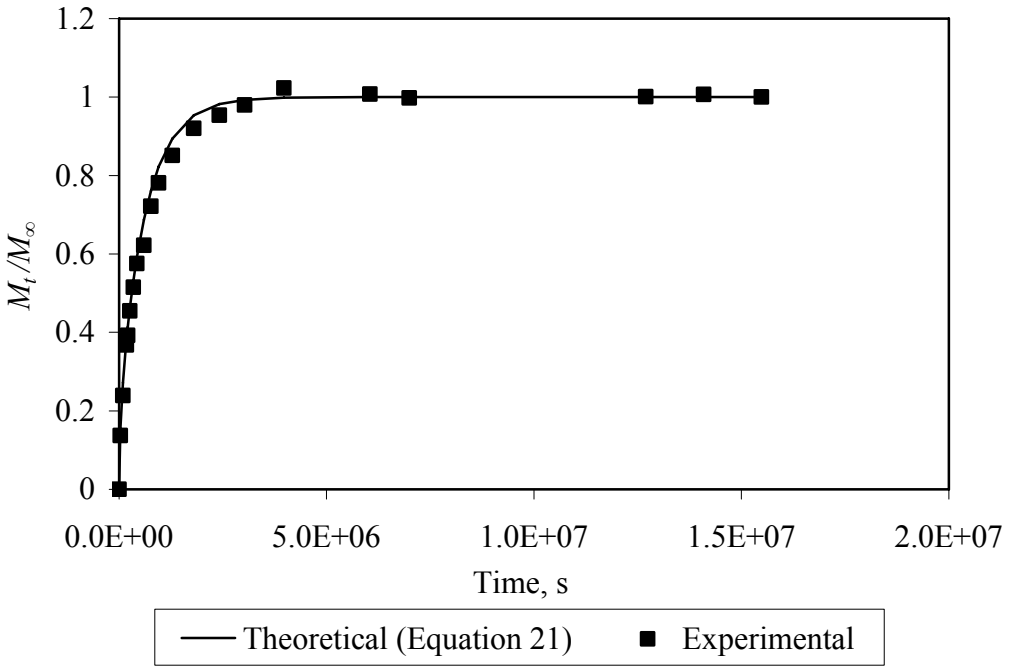

Figure E24. Theoretical and experimental fractional uptake vs. time for epoxy adhesive with 40 wt% rubber in 1 M NaCl solution.

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